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RECENT ADVANCES IN THE CHEMISTRY AND BIOLOGY OF SEA WATER

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RECENT ADVANCES IN THE CHEMISTRY & BIOLOGY OF SEA WATER

BY

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This book summarizes, clearly, concisely and with authority, the large amount of important work that has been done in recent years on the relation of plant and animal life in the sea to the chemical constituents of sea water. Much of this work has, in fact, been carried out by Dr Harvey himself and other members of the staff of the Marine Biological Laboratory at Plymouth, since the publication of Dr Harvey's earlier book (in 1927) This new material will be essential to all marine biologists, both in England and the U S.A., and will also afford the best outline of an important part of active biological work for the ordinary biologist and advanced student

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H. W. HARVEY

MARINE BIOLOGICAL ASSOCIATION
PLYMOUTH, 1943

I. INTRODUCTION

THE salt content of water from the open oceans, away from the immediate influence of melting ice or rivers, rarely exceeds 3·8% and is rarely less than 3·3%. Nine kinds of ions constitute 99½% of the salts in solution; these are found in remarkably constant proportion, the one to the other, unless the water is of unusually low salinity. On the other hand, some of the minor constituents and dissolved gases are found in widely differing proportion, due to the activity of living organisms. The organisms concentrate some elements in their tissues and body fluids; they adsorb other elements on their surface.

Changes in salt content of ocean waters, with position, depth and time, are brought about in the main by greater evaporation taking place in subtropical latitudes and greater precipitation in polar seas. Wind, temperature differences, evaporation and precipitation give rise to currents, causing horizontal transport, most marked and rapid in the upper few hundred metres. Wave motion, convection currents, and turbulence set up by currents passing over an uneven bottom, give rise to vertical mixing. Considerable quantities of water upwell to take the place of water which is passing away as a current in some areas. It is evaporation, precipitation and movement, both horizontal and vertical, which regulate the distribution of salinity; simple diffusion of the salts in solution is extremely slow.

CONCERNING MIXING AND HORIZONTAL TRANSPORT

In order to present a picture of the constitution of sea water and the changes taking place in it in nature, some consideration must be given to the transport of water in ocean currents and the forces which either enhance or restrain mixing. This is equally necessary in any attempt to present the converse picture of how variations in the water affect the organisms and affect, even control, the fertility of the seas.

It is convenient to take the Atlantic Ocean as an example. The salt content of the waters is indicated in Figs. 1 and 4. In high latitudes the salinity of the upper layers is frequently less

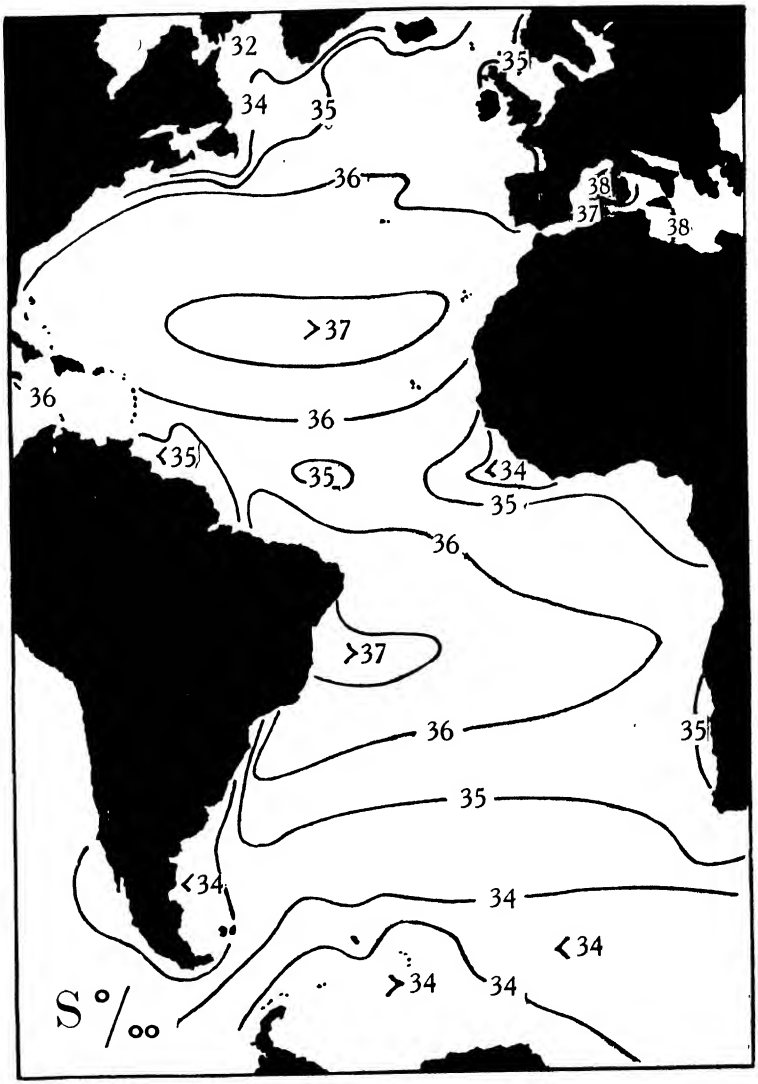

FIG. 1. The salinity, in grams per kilo, of the surface water of the Atlantic Ocean.

than the salinity of the water below. The run-off from melting ice or the land fans out on the surface and sets up a current which is deflected by the earth's rotation and also grows deeper as it picks up water from below. In lower latitudes the salinity is usually greater in the upper layers; here evaporation has concentrated the water at the surface.

A complex system of currents is set up in the upper layers caused by wind, temperature differences, evaporation and precipitation (Fig. 2). Friction and the force of the earth's rotation influence their direction.

This force tends to deflect the current to the right in the northern hemisphere. It is directly proportional to the velocity of the current. At the equator the force is zero, while in high latitudes it may attain considerable magnitude; it varies with the sine of the latitude.

A vertical cross-section through a current in the northern hemisphere, seen in the direction of the current, shows that the light forward-moving water is deeper on the right-hand side of the current, where it accumulates against some other water mass or natural boundary. The density surfaces slope downwards towards the right, equilibrium being attained when the forces which tend to restore them to the horizontal are strong enough to balance the force due to the earth's rotation.

Hand in hand with this deepening and piling up of water on one side of a current, water is picked up and taken into the current as it progresses.

A noticeable effect of the earth's rotation is also seen where rivers run into the sea; the diluted sea water moving out from the coast tends to turn right in the northern hemisphere.

By carrying water away, the ocean currents lead to water upwelling from below to replace it (Figs. 2 and 4). Where upwelling penetrates into the surface layers and keeps them replenished with the phosphate and nitrogen salts required for plant growth, both plant and animal life is singularly abundant.

In addition to horizontal transport in the currents and the upwelling of great volumes of water in particular areas, mixing, both vertical and horizontal, is caused by turbulent motion.

As with upwelling, vertical mixing due to turbulence (the vertical component of *eddy diffusion*) refreshes the upper sun-lit

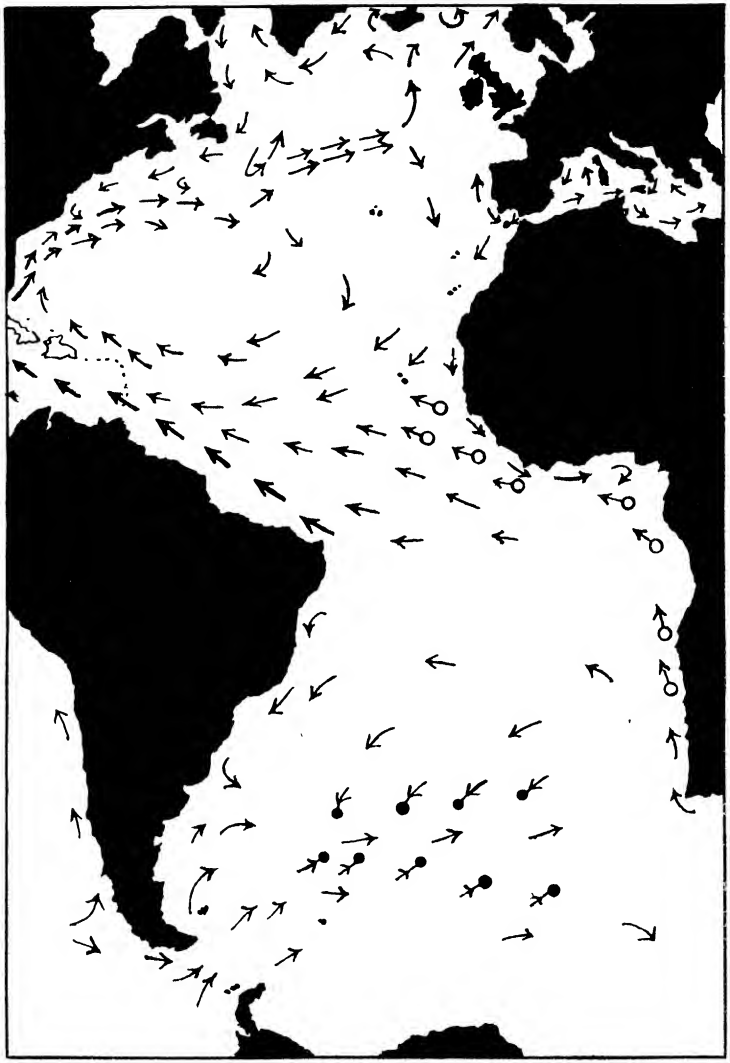

FIG. 2. The currents in the upper layers of the Atlantic Ocean. Arrows arising from a circle indicate water upwelling from below; arrows leading to a dot indicate water sinking below the upper layers.

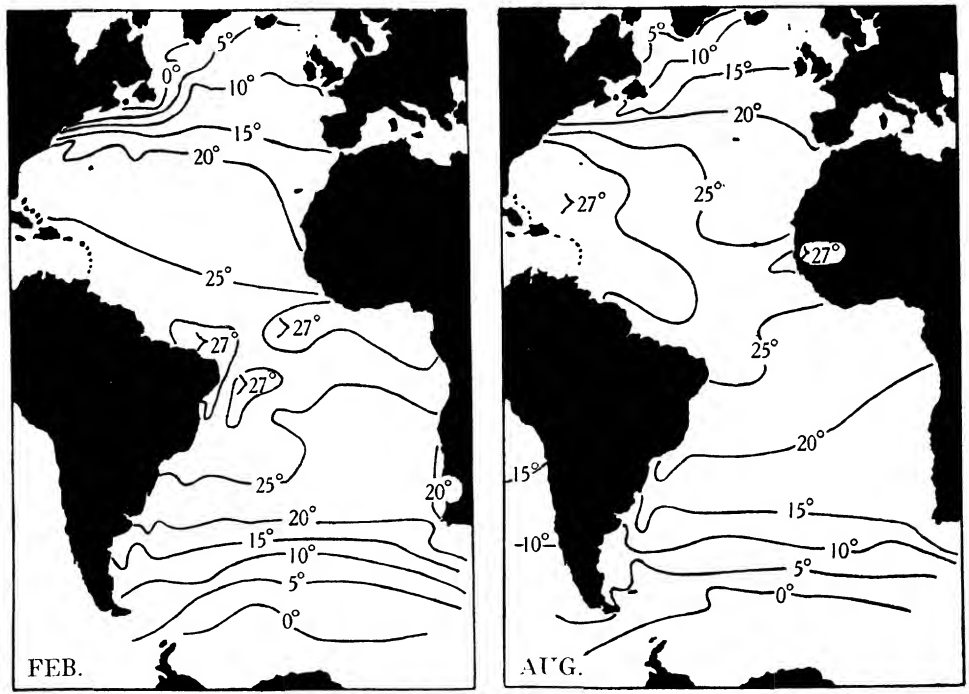

FIG. 3. The surface temperature, in degrees Centigrade, of the Atlantic Ocean during February and August.

layers with the nutrient salts required for plant growth. It also plays a predominating part in restraining the movement of one layer over another, since it causes frictional resistance (*eddy*

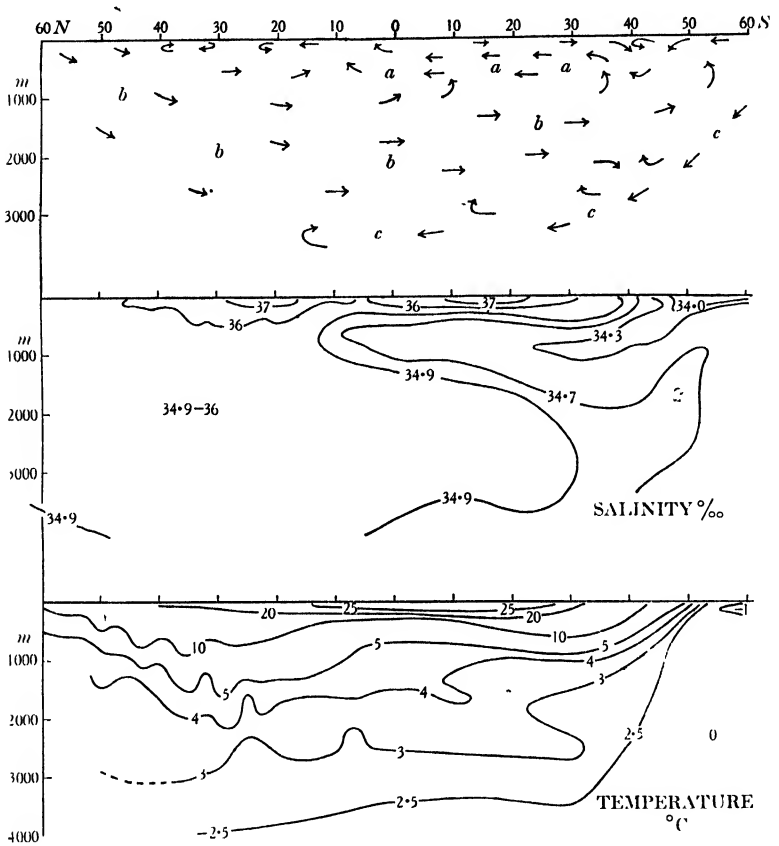

FIG. 4. Sections from 60° N. to 60° S. along the 30° W. meridian of longitude, showing the general trend of the currents, the salinity in grams per kilo and the temperature in degrees Centigrade. *a*, *a*, *a*, the 'Antarctic Intermediate Current'; *b*, *b*, *b*, the 'Atlantic Deep Water'; *c*, *c*, *c*, the 'Antarctic Deep Water'. The depths are shown in metres.

viscosity). It carries heat from warmer to cooler water. Unfortunately it does not lend itself to direct measurement.

Eddy diffusion is set up (*a*) by wave motion at the surface; the orbital motion falls off with increasing depth, the decrease being less rapid in the open oceans with waves of greater

distance from crest to crest, (*b*) by convection currents set up by cooling and evaporation at the surface, (*c*) by currents passing over an uneven bottom, the turbulence so caused decreasing with increasing distance above the bottom. Turbulence developed in this way by to-and-fro tidal currents in relatively shallow seas often keeps the waters mixed vertically throughout the year. It is particularly noticeable where the current meets a hill or passes over a cliff in the bottom; then turbulence may be sufficiently great to cause ripples at the surface on a calm day some 100 to 150 metres above the bottom.

A secondary result of turbulence set up at the bottom is, by increasing frictional resistance in the water above, to cause a superficial current to change its course. An area of the sea where turbulence is relatively great acts as a natural boundary to an ocean current. Such areas are found where the deep ocean floor rises to the submarine plateau which surrounds the continents and are also found over submarine ridges. Such a ridge runs down the centre of the Atlantic; the path of the weakened westerly drift of the Gulf Stream is undoubtedly influenced by this, and the main flow towards Europe passes over it where the depths are greatest. The main current or drift of water into the Norwegian and Barents Sea likewise passes over the submarine ridge lying between Scotland and Iceland where the depths are greatest—that is, through the Faroe-Shetland Channel. In this way the contour of the sea floor has a marked influence on the direction of currents in water far above it.

Yet another type of motion takes place within the sea. The level, at which some particular temperature or salinity occurs, oscillates up and down. The range may exceed 200 metres at mid depths in the open oceans. These *internal waves* will presumably enhance eddy diffusion.

The waters of the oceans are never still. It is only in some adjacent seas, cut off from the circulation of the oceans by a submarine ridge, that stagnant deep water is found. Such occurs in the Black Sea and some Norwegian fiords, where, as a result, the deep water becomes deoxygenated and sulphides are formed.

It remains to consider the conditions which damp down or hinder vertical eddy diffusion, that is, conditions which lead to *stability of the water column.*

Where the density of the water increases rapidly with depth, due to increasing salinity, decreasing temperature, or both, considerable work is required to mix the lighter water with the heavier water below. The vertical component of eddy motion is restrained and vertical eddy diffusion hindered. In low latitudes insolation warms the upper layers, and below a depth of some 100 metres there is usually a rapid decrease in temperature. Over the Sargasso Sea, the warm water, forced in from the encircling Gulf Stream system of currents, extends to greater depths. A layer of rapidly increasing density is known as the *thermocline* or *discontinuity layer*. In temperate and often in high latitudes, a thermocline is set up during the summer months, unless turbulence is so great that it never gets a chance of becoming established. This may happen in shallow seas with strong tidal currents, or in open oceans where a succession of gales follow each other. Over great tracts of the Southern Atlantic in the area of the Roaring Forties no thermocline develops in summer, whereas at an equal distance from the equator in the northern hemisphere a well-marked thermocline is set up.

It was at one time thought that the water above a well-marked thermocline was almost entirely cut off from the water below in respect to upward diffusion of dissolved salts, but some recent observations may lead to a modification of this view. However, only a sparse population of plant life is encountered above a marked thermocline which has persisted for any length of time, for the plants rapidly utilize the nutrient salts in the water and are left with an insufficient supply to maintain rapid growth.

The presence of a thermocline may have other far-reaching effects. Owing to reduced eddy viscosity the water above slides more readily over the water beneath, and horizontal transport is favoured. As a result of such movement, a change in salinity is often found at the thermocline.

It is interesting to follow the establishment and disappearance of a thermocline in temperate areas. In the semi-enclosed waters at the mouth of the English Channel, where the distance from crest to crest of the waves is relatively short compared with the open ocean, a strong well-marked thermocline develops at 13 to

14 metres in May or June when the weather is reasonably calm. A summer gale sends it down to some 18 metres, or more, and subsequent hot calm weather may allow a second thermocline to develop above the first. The level at which the thermocline persists varies from year to year around an average depth of some 15 or 16 metres. Its level, or depth below the surface, oscillates up and down some 2 metres due to internal waves. Towards the end of August the surface starts to lose more heat than it gains from insolation; this loss is due for the most part to evaporation. The upper warm layer cools gradually and the first autumn gale breaks down the thermocline. Then there is rather complete mixing of the water from top to bottom. The sequence of events is shown in Fig. 5.

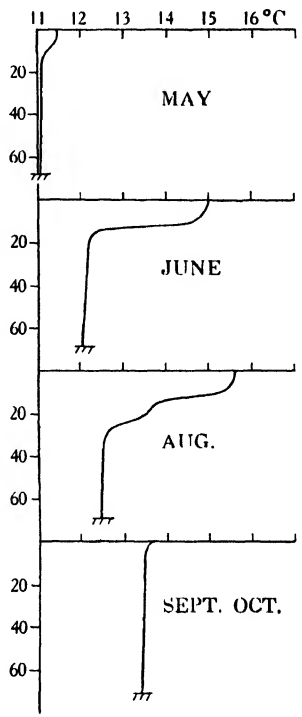

Fig. 5. Diagram illustrating the establishment and disappearance of a thermocline at a position in the English Channel. Depth 70 metres.

Further seaward, in water having a depth of 2000 to 3000 metres, the data available indicate that the thermocline is formed in summer at a deeper level, at some 25 to 30 metres. Here the waves are longer from crest to crest, and the orbital motion which they set up will extend deeper. Fig. 6 shows the distribution of temperature with depth in June at a position some 350 miles south-west of the entrance to the English Channel. It may be inferred from it that when the thermocline breaks in autumn, mixing takes place to a considerable depth at this position in the open ocean.

These considerations indicate mechanisms by which the waters in the oceans are mixed with the water above and below. As a mass of water proceeds in a current, mixing also takes place with the water on either side; yet such a water mass may retain

characteristics, as having a salinity and temperature higher than that of the surrounding water, for some years—completion of horizontal mixing is very slow.

It is of interest to consider some differences between the open ocean and shallow inshore waters.

On approaching the coast of the continents from the deep water of the open oceans, the depth usually shoals rather rapidly from over 2000 metres to some 200 metres. This *continental slope* is frequently no more than 150 miles in width, except in the Arctic and between Europe and Greenland, where there are large tracts with depths intermediate between these values. The *continental shelf*, with depths of less than 200 metres, may extend to a width of many miles and covers more than 6 % of the entire area of oceans. On passing the continental slope and proceeding over the shelf, the clear blue of the deep ocean changes to a more green hue, particularly in temperate and high latitudes. The amount of minute living organisms and particles of organic debris in the water becomes greater. The fauna living on and in the bottom plays a larger part in the changes taking place in the whole water column as the depths decrease over the continental shelf. Debris from dead organisms breaks down relatively quickly on reaching the bottom, and nutrient salts used by plants are regenerated nearer the surface than in deep-water areas. The bottom frequently contains a rich fauna, some 100 g. of living tissue composed of worms, protozoa and molluscs being no unusual quantity on and in a square metre of mud bottom. On nearing the coast, particularly where the sea is shallow and rivers enter the sea, the water is diluted and holds increasing quantities of sediment in suspension. The water is

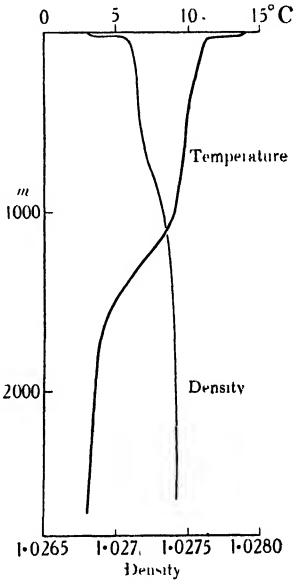

FIG. 6. Diagram showing the change in temperature and in density with depth at a position in the Atlantic, 360 miles south-west of the English Channel.

discoloured, its transparency reduced and the layer or zone in which there is sufficient light for plants to grow becomes thinner. Such 'inshore' conditions may extend many miles seaward over shallow depths, as in the southern North Sea, where tidal currents cause much vertical mixing and keep much sediment in suspension. During summer the whole column of water warms and there are no cool depths as farther out to sea (Fig. 7). During winter there is a tendency for the diluted water

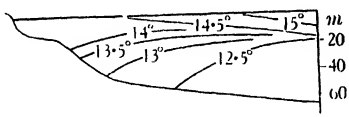

FIG. 7. Section, extending 20 miles south-west from Plymouth, showing the distribution of temperature (7 August 1924).

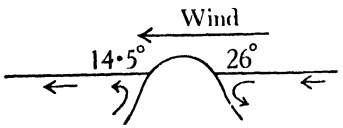

FIG. 8. Section showing how currents due to offshore winds affect the temperature of the surface water to leeward of the Galapagos Islands.

to remain banked up near the coast, running out as a surface layer during summer, when strong offshore winds may also blow the warm water seaward, cooler subsurface water from offshore replacing it. Thus the inshore animals are subjected to a considerable annual range of salinity and temperature, with rather rapid changes. It is of interest that the distribution of many marine animals is limited by the range of temperature and has been linked with the salinity of the water, and it is remarkable that some species of fish are able to perceive very small differences not only in temperature but also in salinity, as little as 0·06 g. per kilo in water containing some 35 g. per kilo.

On passing up an estuary, a more or less rapid change in salinity is encountered. Since the dissolved salts in river waters are different in composition from those in sea water, the composition of the dissolved salts very gradually changes. In some estuaries, particularly where the bottom is uneven and there is a strong tidal flow, the water is kept well mixed. In others the fresher water flows out over more saline water, picking up water from below and carrying this out with it. This leads to a countercurrent being set up near the bottom (Fig. 9). Where there is an

increase in salinity with increasing depth in an estuary, even where the whole mass of water moves up and down the estuary with the tide, there is a residual upstream movement of the bottom water due to this mechanism. Conditions in the River Tees estuary, which is of this type, have been very fully investigated. The diagrams in Fig. 10, made from a great number of observations extending over several years, show the distri-

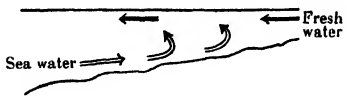

FIG. 9. Diagram illustrating the countercurrent set up in estuaries where less saline water flows seaward in the upper layers.

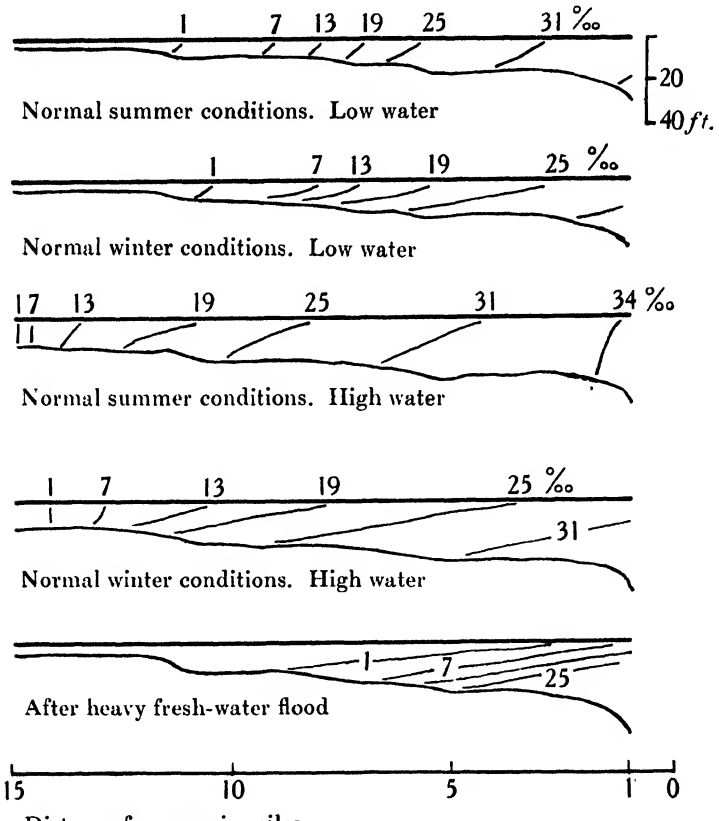

FIG. 10. Diagram illustrating the distribution of salinity in the estuary of the River Tees. (After Alexander, Southgate & Bassindale.)

bution of salinity at low and high water during summer and in winter, when the flow of fresh water is greater. Measurements with floats and meters showed that the ebb tide was strongest in the surface layers and that the water ran out at the surface for a longer period than it flooded in, whereas the flood tide was strongest in the deeper layers where the water ran in for a longer period than it ebbed out.

A large quantity of organic matter is discharged into this estuary at various points between 5 and 11 miles from the sea, mainly at low water. In consequence of the rapid bacterial

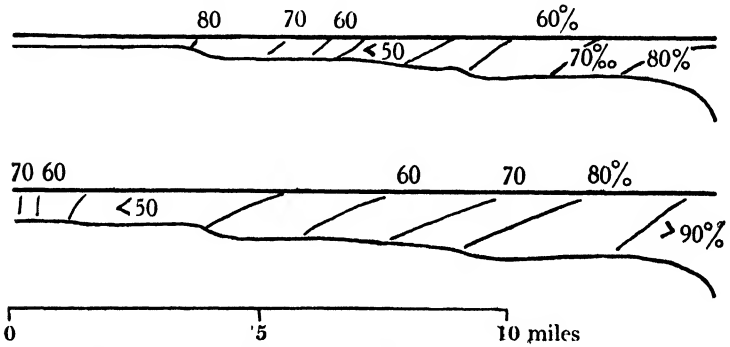

FIG. 11. Diagram showing the percentage saturation with oxygen of the water of the Tees Estuary, under summer conditions, the temperature of the water being 13° to 16° C. (After Alexander, Southgate & Bassindale.)

breakdown of this organic matter, the oxygen content of the water is reduced. The degree to which this reduction takes place is mainly controlled by the temperature of the water. Fig. 11 shows how the oxygen-depleted water is moved bodily up and down stream with the flow and ebb of the tide.

CONCERNING MARINE ORGANISMS

Changes in the composition of the sea salts are brought about almost exclusively through the agency of plants, animals and bacteria, while interchange with the atmosphere and the agency of living organisms control the quantities of gases in solution.

Sea water cannot be considered merely as a solution of salts without regard to the organisms in it. Even storage in a bottle brings about notable changes in its composition after one or two days in the light or in the dark.

The activities, distribution and conditions controlling the growth of marine organisms constitute the science of Biological Oceanography, with which any study of sea water is intimately linked. Several terms peculiar to this branch of natural history crop up throughout the literature dealing with sea water. For the purposes of this book it is convenient to define some of these terms in a form which may serve as an introduction to part of the subject-matter or underlying theme.

The greater part of the flora and much of the fauna of the ocean consist of *plankton*. These are organisms which live suspended in the sea and have not sufficient swimming power to stem the currents. They vary greatly in size from large jellyfish to bacteria and minute protozoa. The smallest are termed *nannoplankton*, a loose term embracing those which are not retained by the finest silk nets. *Phytoplankton* organisms constitute the plant life of the open oceans, beyond the narrow fringe where attached seaweeds grow. These plants absorb carbon dioxide from solution, and set free oxygen. They absorb salts from the water, notably phosphates and salts containing nitrogen, converting them into organic compounds. They absorb on their surfaces various ions in solution, as those of gold, silver and other heavy metals. They need no supply of organic food. The smallest measure some 3μ (0·003 mm.) across, and few species contain more living tissue than the volume of a pin's head. In temperate and Antarctic seas the majority, in bulk if not in numbers, are usually but not always retained by a net having meshes $40 \times 50\mu$. In tropic and Arctic seas the bulk of the plant life is often nannoplankton.

The majority of species of phytoplankton belong to four groups. *Diatoms* are unicellular plants with perforated siliceous external skeletons, partly filled with protoplasm which is thought to stream out through the perforations and present a naked surface to the water. Chloroplasts containing chlorophyll, carotins and fucosan —the colouring matter of brown algae—lie embedded in the protoplasm, which often contains highly refractive globules, composed mainly of fatty acids, and constitute the plants food reserve. Diatoms abound in temperate seas, particularly during spring and to a lesser extent during autumn, in polar seas during summer, while in tropic seas they are less numerous. Under suitable con-

ditions they grow rapidly; some species are capable of doubling their numbers every 24 hours. Chlorophyll-containing *peridineans* or *dinoflagellates* are unicellular organisms, with chitinous exoskeletons. They are widely distributed and sometimes form the bulk of plant life during summer in temperate regions. *Coccolithophores* are unicellular plants of very small size with calcareous skeletons. They are particularly numerous in tropic seas. The phytoplankton also includes chlorophyll-containing *flagellates*, many species about 3 to 4 μ in diameter, and others smaller.

These small phytoplankton organisms constitute the food upon which all marine animal life depends. They are remarkable for their capacity of very rapid growth. Although the quantity of plants below a square metre of the sea may be very small, the production during the course of a year amounts to a considerable quantity; in many areas it would not be exceeded by the annual production on a square yard of cultivated field. The quantity of phytoplankton present at any time is kept low by animals grazing it continuously, and frequently by shortage of available nitrogen and phosphorus.

They build up their cell substance while in the upper layers of the sea, within the *photosynthetic zone* or layer where there is sufficient light. This layer extends from the surface to the *compensation point*, below which the plants lose more by respiration than they gain by photosynthesis. The depth of the photosynthetic zone varies throughout the day with the intensity of illumination. The average depth throughout 24 hours varying from 100 metres or more in clear tropical waters to 30 to 50 metres in summer or 10 to 20 metres in winter in temperate regions. In turbid inshore waters it may not exceed 1 to 2 metres in depth. Transparency of the water, freedom from debris and organisms, play a leading part in controlling the depth of the photosynthetic zone.

The *zooplankton* includes a great variety of animals; a large proportion are crustacea, many of which are herbivorous, living on the phytoplankton. A few species of free-swimming animals are also herbivorous at times, but it is the planktonic herbivores which constitute the great grazing population of the sea. Many species of zooplankton rise into the upper layers at night and sink below the photosynthetic zone by day.

Many species of zooplankton are naked, others have external skeletons of chitin, while a few, which however may occur in great numbers, are reinforced with calcareous or siliceous structures. Bottom deposits in tropical and subtropical waters are often characterized by the calcareous skeletons of *Globigerina*. Extensive tracts of the floor of the southern ocean are also covered with an ooze containing the broken siliceous skeletons of diatoms.

Marine animals, both planktonic and free swimming, feeding on phytoplankton or each other, excrete carbon dioxide, phosphate, ammonium and soluble organic matter into the water. They adsorb on their surfaces several ions occurring in solution in the water, and certain species are found to be rich in some particular element, as vanadium or strontium or copper.

Species of both animals and plants which occur most abundantly near land are termed *neritic*, in distinction to *oceanic* species which are most abundant away from the influence of land.

Further information concerning the subjects dealt with in this Introduction may be found in *The Oceans, their physics, chemistry and biology* by Sverdrup, Johnson & Fleming (1942), in *The Seas* by Russell & Yonge (1928) and in *The depths of the Ocean* by Murray & Hjort (1912).

II. 'SALINITY', 'CHLORINITY', SPECIFIC GRAVITY

THE exact estimation of the salt content of sea water, by the direct method of drying and weighing, presents difficulties. The sea salts are tenacious of moisture; at temperatures necessary to drive off the last traces, bicarbonates and carbonates are decomposed and bromine with some chlorine is set free and lost. On the other hand, the chloride + bromide content can be measured exactly, since they are completely precipitated as the silver salts. Hence two conventions have arisen, embodied in the terms 'Salinity or S $^{o}/_{oo}$' and 'Chlorinity or Cl $^{o}/_{oo}$'.

Knudsen (1902) defined the salinity of a water as the weight in grams *in vacuo* of solids which can be obtained from water weighing 1 kilogram *in vacuo*, when the solids have been dried to constant weight at 480° C., the quantity of chloride and bromide lost being allowed for by adding a weight of chlorine equivalent to the loss of the two halides during the drying.

Thus the salinity equals the weight of the total salt per kilo of water, less most of the weight of the bicarbonate and carbonate ions and less the difference between the bromine and its equivalent of chlorine. An ocean water contains about 0·45 % more salts than its salinity value.

The halogens precipitated by a silver salt can be estimated with precision, the precipitate consisting of silver chloride and bromide with an insignificant trace of iodide. This brought into use the term 'Chlorinity', by which was understood the mass of chlorine equivalent to the mass of halogens contained in 1 kilogram of sea water. This definition implies a knowledge of the exact atomic weights of chlorine and silver. Since the adopted atomic weights have changed from time to time, 'Chlorinity' has been redefined (Jacobsen & Knudsen, 1940) in terms of the weight of silver precipitated:

$$\text{Cl } {}^{o}/_{oo} = 0{\cdot}3285234 \text{ Ag}.$$

The relation between chlorinity and salinity has been investigated by Knudsen (1902) for a number of sea-water samples

covering a wide range of salinity, those of lower salinity being collected from the Baltic where incoming ocean water is diluted with river water containing small quantities of salts in solution. A straight line relation was found, where

$$S\ {}^{\circ}/_{\circ\circ} = 0{\cdot}030 + 1{\cdot}8050\ Cl\ {}^{\circ}/_{\circ\circ}.$$

When an ocean water is diluted with distilled water or ice-melt the resulting low salinity waters will not have exactly the same density, conductivity and composition as natural Baltic waters of equal chlorinity, from which the above relation was derived. This relation forms the basis of the tables in general use linking chlorinity with salinity and density.

Present knowledge of the circulation of the water masses occupying the oceans, and much of our knowledge of currents in the upper layers, rests upon small differences in salinity and very small differences in density of the water *in situ*. In practice both are calculated from the chlorinity.

Differences in chlorinity between two samples of water can be estimated with considerable accuracy by titration with silver nitrate, using chromate as indicator and following the customary technique. It is usual to titrate a 'Standard Sea Water', whose chlorinity has been determined by both gravimetric and volume-weight analyses, and so obtain the difference in chlorinity between the unknown and the standard. Sealed tubes of such 'Standard Water' may be obtained from the Laboratoire Hydrographique, Copenhagen; by this arrangement workers in different countries have the same basis for comparison.

A description by Matthews of the method usually employed is given, since the accuracy of the estimation depends so much on the smaller details; this description supplements that by Oxner & Knudsen (1920).

The pipette generally used is of the Knudsen pattern, with a three-way tap instead of a mark; water is sucked up through one branch and allowed to flow out by admitting air through the other. The upper stem should be long enough to allow of the pipette being held by it without heating the bulb, and the lower should reach to the bottom of the sample bottle. The capacity may be from 10 to 15 c.c.; it need not be known with the highest accuracy since the method is purely comparative. When running the water out it should be held vertically, and as soon as it is empty except for the drop at the bottom the point should be held against

the side of the tumbler for some invariable length of time, say 10 seconds. When clean, such a pipette is accurate to about one part in four thousand. Ostwald's tap grease is the best, but there is no kind that does not soil the pipette sooner or later.

The burette is of the bulb form; the larger part of the capacity is expanded into a bulb at the top so as to decrease drainage errors. Instead of a zero mark there is a fine jet; each time the burette is filled a little of the silver solution is allowed to overflow. The unit of graduation is equal to 2 c.c. and the graduation is from 16 to 21·5 or from 18 to 24 units, corresponding to salinities of about 27·9 to 38·8, or 32·5 to 43·3. The length of a graduated unit should be about 4 cm. and should be divided into 20 parts. The burette may be provided with glass taps. A much more convenient method is to use thick-walled rubber tubing (pressure tubing) and strong screw clips. A wooden stand is better than a metal one, and should be made to support the rubber firmly on both sides of the clip. With such an arrangement the burette will remain clean for years, except for a slight dark deposit of reduced silver which does no harm. The calibration of course should be done with the greatest accuracy.

The silver nitrate solution should be made from the fused salt, in order to avoid any trace of acidity, and should be of such a strength that when a pipetteful of the standard is titrated the burette reading is the same as the 'chlorinity' marked on the sealed tube within 0·145. The standard generally contains about 19·38 parts per thousand of chlorine; in this case, with a 10 c.c. pipette, the silver nitrate solution should contain 24·50 g. per litre.

The indicator is a 10% solution of neutral chromate of potash.

The standard water (normal water of the International Council) is emptied from a sealed tube into bottles of the kind used to hold the samples, generally 6 or 7 oz. milk bottles closed by porcelain stoppers and rubber washers held down by swing catches of wire. The bottles are allowed to stand for some hours, or better overnight, near to the burette and stock solution, so that everything takes the same temperature. Exposure to the rays of the sun or any other source of irregular heating should be carefully avoided. Four pipettefuls of standard water are measured into the first four glasses, and then the samples to be analysed. All should thus be at the same temperature. One of the standard waters is then analysed. Two drops or more of the indicator are added to the water in the tumbler, and the silver nitrate is run in with constant stirring, quickly at first, and then slowly as the red colour becomes more lasting. Finally it is added a drop at a time until the red colour is permanent for half a minute. It is better to titrate to the first slight change in colour of the precipitate, not much more than a slight soiling, rather than to a distinct red. Ten of the samples are then titrated, then a standard, and so on. The advantage of measuring out a number of standards and samples at the beginning is that it is possible to break off the work when only half done if necessary, and resume it later without causing any inaccuracy. The results of course are read in silver per volume of water. They must be calculated to weight, and this is easily

done by the corrections given in Knudsen's Tables, provided that the silver nitrate has been made up of the correct strength within 0·15.

The method is very accurate when once it has become mechanical, and a difference of more than 0·01 Cl $^{o}/_{oo}$ between duplicates is a sign of something wrong, generally either grease in the apparatus or a chipped point on the pipette. Sea water of low salinity, less than 20, need not be analysed with quite the same accuracy as a rule, and a good cylindrical burette of the ordinary pattern is sufficient.

The accuracy depends upon the pipette and burette draining to the same extent during consecutive estimations. The estimation is tedious, since the latter part of the titration proceeds slowly. Keys (1931) uses a temperature compensated syringe pipette, which delivers with an accuracy of about one part in 15,000, in a rapid and accurate method of the Volhard principle. Miyake (1939) states that a sharper end point is obtained by using as indicator 2 c.c. of a 1 % starch solution containing 0·005 % of the sodium salt of fluorescine, and that this materially reduces the time required for titration.

A method of estimating salinity from electric conductivity measurements has been in constant use in the 'Ice Patrol' vessels of the U.S. Coastguard Service (Wenner, Smith & Soule, 1930), and a method based on measurement of the refractive index of the water has been used to a limited extent. Many methods based on density determinations have been devised, but do not meet the requirement of use on board ship if great accuracy is required.

For many purposes it is sufficient to titrate 10 c.c. of sea water with a solution containing 27·25 g. of silver nitrate per litre from an ordinary burette. The volume, in c.c., of the silver nitrate required will roughly equal the salinity of the sample. Actually

Salinity, S $^{o}/_{oo}$ found	Correction to be applied	Salinity, S $^{o}/_{oo}$ found	Correction to be applied
40	−0·15	22	+0·22
38	−0·08	20	+0·23
36	−0·03	18	+0·23
34	+0·03	16	+0·23
32	+0·07	14	+0·20
30	+0·11	12	+0·19
28	+0·15	10	+0·16
26	+0·17	8	+0·15
24	+0·20		

they are not quite in the same proportion, since 10 c.c. of a more dilute sea water than the 'normal' water will not weigh so much. To allow for this it is necessary to apply the small correction given in the table.

Specific Gravity

The relations between chlorinity, temperature and specific gravity of ocean and of low salinity Baltic waters, determined by Knudsen, are given in his *Hydrographic Tables*. The substantial accuracy of these has been confirmed by subsequent determinations with ocean waters from various parts of the world (Thompson & Wirth, 1931, and others).

It is usual to express the specific gravity of sea water, the ratio of its weight to that of an equal volume of distilled water at 4° C., in abbreviated form, denoted by the letter σ. If 1·02653 is the specific gravity of a water at t° C., this is expressed as $\sigma_t = 26{\cdot}53$. The following figure shows the variation of specific gravity with salinity and temperature.

The effect of pressure on the specific gravity, such as exists at great depths in the ocean, has been investigated and tables have been drawn up from which the correction may be found (Ekman, 1910).

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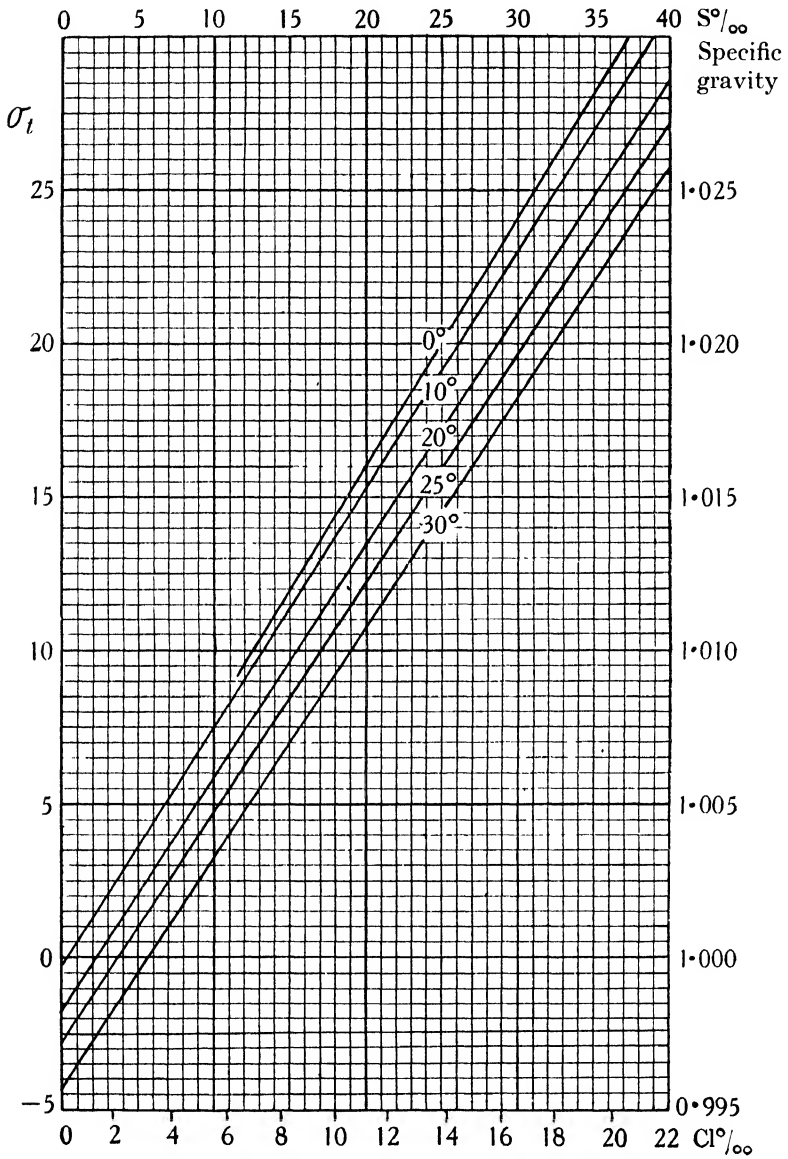

FIG. 12. The relation between salinity, chlorinity and specific gravity at 0°, 10°, 20°, 25° and 30° C.

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III. THE MAJOR CONSTITUENTS

THE sea salts of ocean water, away from any considerable dilution by land drainage, are of almost constant composition. Dittmar's analyses of seventy-seven samples of water collected by H.M.S. *Challenger* in 1873–76 from all the oceans showed this constancy. Subsequent analyses, in greater detail, bear out Dittmar's very accurate data. These have been recalculated in terms of the atomic weights of 1939 by Lyman & Fleming (1940).

A few of the minor constituents, such as nitrogen compounds and phosphates, undergo considerable changes since they are utilized by plants. Small changes in the calcium content are brought about in the same way by animals and plants, and also by solution of calcium carbonate from calcareous bottom deposits at great depths.

When ocean water is diluted with land drainage, the percentage composition of the contained salts is altered, since river water contains more sulphate than chloride and more calcium than magnesium than sodium. This change is reflected in Knudsen's formula relating the salt content to the chlorinity, where

$$S\ {}^{o}/_{oo} = 0{\cdot}030 + 1{\cdot}8050\ Cl\ {}^{o}/_{oo}.$$

The following table gives the percentage composition of salts in sea water, which has not been materially diluted by land drainage. It is compiled from the recalculated data of Dittmar, and various subsequent analyses which show the relation of one or other constituent to the chlorinity of the water.

Percentage composition of salts in ocean water

Na^{+}	30·4 %	$'Cl$	55·2 %
Mg^{++}	3·7	$''SO_4$	7·7
Ca^{++}	1·16	$'Br$	0·19
K^{+}	1·1	H_3BO_3	0·07
Sr^{++}	0·04	($'HCO_3$ and $''CO_3$	0·35)

Minor constituents 0·02–0·03

In sea water the carbon dioxide is mostly in the form of bicarbonate and the boric acid as undissociated molecules (p. 54).

The more recent data concerning these major constituents are given in the following account.

Sodium. In the early analyses of sea water, the sodium was found by difference. Recently the ratio of sodium to chlorinity has been found directly by precipitation with zinc uranyl acetate: Webb (1938) obtained a value of $0{\cdot}5549 \pm 0{\cdot}001$ for the ratio, while Robinson & Knapman (1941) found 0·5549 for waters of the North Pacific and a slightly greater ratio for inshore waters.

Magnesium. Dittmar's analyses recalculated by Lyman & Fleming (1940) give the ratio of magnesium to chlorinity as 0·06801. Thompson & Wright (1930) cite a number of analyses by other observers, and themselves found a mean ratio of 0·06694.

Matthews & Ellis (1928), by precipitating the magnesium with 8-hydroxyquinoline, found a mean ratio of 0·06785 in the Eastern Mediterranean and 0·06814 in the Gulf of Aden.

Miyake (1939) finds ratios of 0·0669 and 0·0676 for the North-East and West Pacific respectively.

Wattenberg & Timmermann (1937) find the solubility product of both magnesium carbonate and hydroxide to be greater in sea water than in fresh water,

$$K'_{Mg(OH)_2} = 5 \times 10^{-11}, \quad K'_{MgCO_3} = 3 \times 10^{-4}$$

for ocean water.

When the hydrogen-ion concentration of sea water falls and the *p*H rises above *circa* *p*H 9, magnesium hydroxide separates as a precipitate with calcium carbonate.

Calcium. In waters of the open ocean away from the influence of land drainage, the calcium content of the water bears an almost direct relation to the chlorinity; very slight divergences are caused by organisms utilizing calcium in the upper layers and by solution from bottom deposits as a result of pressure at great depths.

The relation of calcium to chlorinity found by various observers is shown in the following table, in which allowance has been made for the strontium included in the estimates for calcium (Webb, 1938):

	Ca/Cl
Dittmar (1884) recalculated using 1938 atomic weights (Lyman & Fleming, 1940)	0·02095
Thompson & Wright (1930)	0·02090
Thompson & Wright, average of estimates by other observers	0·02177
Kirk & Moberg (1933)	0·02122

When ocean water is diluted with river water, the ratio is affected, since river water usually contains very much more calcium in proportion to chloride than sea water. In low salinity waters of the Baltic (Cl $^{o}/_{oo}$ 1 to 7) several distinct water masses have been distinguished by their Ca/Cl ratio (Gripenberg, 1937).

The quantity of calcium which can exist in solution in sea water is limited by the solubility of calcium carbonate. If the concentration of carbonate ions is raised, as by blowing a current of alkali-washed air through the water, calcium carbonate is precipitated. Considerable supersaturation may be attained before precipitation commences. At high *p*H values some magnesium hydroxide also separates.

The solubility of calcium carbonate is greatly increased by the presence of neutral salts. The 'apparent' solubility product ($K'_{CaCO_3} = C_{Ca''} \times C_{CO_3}$, where $C_{Ca''}$ etc. is the concentration of the ion in gram ions per litre) has been determined (Wattenberg, 1933, 1937) by shaking calcite with sea waters made acid with carbon dioxide, the following values being found at 20° C.:

Salinity $^{o}/_{oo}$	0	5	15	20	25	30	35
K'_{CaCO_3}	0·003	0·05	0·10	0·17	0·25	0·35	$0{\cdot}58 \times 10^{-}$

The variation with temperature for water at S $^{o}/_{oo}$ 32 has been determined in the same manner by Wattenberg & Timmermann (1936):

Temperature ° C.	0°	10°	20°	25°	30°	35°
K'_{CaCO_3}	0·83	0·74	0·62	0·52	0·44	$0{\cdot}40 \times 10^{-6}$

The concentration of carbonate ions in a sea water can be calculated from the following formula, derived from the definitions of carbonate alkalinity and the second apparent dissociation coefficient of carbon dioxide (pp. 59, 64):

$$C_{CO_3} = \frac{\text{'Carbonate alkalinity'} \times K'_2}{2K'_2 + C_H}.$$

Precipitation of calcium carbonate from supersaturated sea water brings about a shift in the carbon-dioxide system, since both free base and total carbon dioxide in solution are reduced. This causes a rise in the hydrogen-ion concentration. Calculated changes agree well with those observed (Wattenberg, 1933, p. 215).

Revelle (1933) has also investigated the 'apparent' solubility product of $CaCO_3$ in sea water, by finding the quantity of calcium remaining in the water after part had precipitated. Air freed from CO_2 was bubbled through samples of water at 30° C. for several weeks, washing out some of the carbon dioxide and causing precipitation of aragonite. At the end of the experiments, the *p*H, excess base, chlorinity and calcium content of the samples were determined. The titrations for excess base were made to an end point of *p*H 4·5, that is, some 3×10^{-4} equivalents of acid were required in excess of the amount required to neutralize the excess base. In order to bring the results into line with Wattenberg's values, the solubility products have been recalculated allowing for this and using Buch's values for K'_B and K'_2.

*p*H	Cl ‰	C_{Ca} mols per litre $\times 10^{-3}$	Excess base corr.	$C_{CO''_3}$ mols per litre $\times 10^{-3}$	K'_{CaCO_3} 30° C.
8·98	20·95	10·57	0·81	0·175	1·81
9·12	20·60	10·63	0·92	0·222	2·36
8·83	19·60	10·19	1·01	0·236	2·4

Experimental data from Revelle, R. & Fleming, R., *Proc. 5th Pacific Sci. Congress*, **3**, 1933.

These values for the solubility product, obtained by precipitating aragonite, are much higher than those found by Wattenberg by dissolving calcite. Equilibrium is attained very slowly, and may not have been completed. Calcite is stated to be more soluble than aragonite.

Smith (1941) has shaken samples of sea water for long periods at 30° C. with calcareous bottom deposits. Carbon dioxide in small quantity was set free in some of the experiments, presumably due to biological oxidation, causing solution of aragonite from the bottom deposit. In other experiments the calcium content of the water decreased owing to precipitation. The results indicated a solubility product in the neighbourhood of $K'_{CaCO_3} = 1{\cdot}2$ for 30° C. Similar values have been calculated by Smith from data by Gee, Greenberg & Moberg (1932).

These latter values indicate that the upper layers in the Caribbean are over 100 % supersaturated, even in areas where

deposition of aragonite is proceeding. Wattenberg's values indicate from 300 to 700% supersaturation in such tropical waters, and marked supersaturation in the upper layers in cold latitudes.

With increasing depth and fall in *p*H due to pressure (p. 55) the waters become undersaturated, and there is evidence of solution from calcareous bottom deposits taking place at great depths (p. 60).

Potassium. Recalculation of Dittmar's analyses by Lyman & Fleming (1940) show a ratio of potassium to chlorinity equal to 0·02029. An average value of 0·02000 from various published data is given by Thompson & Robinson (1932). Analyses by Webb (1938) give a value of $0{\cdot}02009 \pm 0{\cdot}00020$. Miyake (1939) found a ratio of 0·0191 in Pacific waters.

The small quantity of potassium in sea water in comparison with that of sodium is considered due to its more ready adsorption on particles of detritus and its consequent concentration in bottom deposits (Goldschmidt, 1934; Noll, 1931). Since living organisms obtain and concentrate potassium from the waters, they may help in this process.

Strontium. Analyses by Desgrez & Meunier (1926), since confirmed (Thompson & Robinson, 1932), show a strontium/chlorinity ratio of 0·0007. A similar value has been obtained by Webb (1938), who points out that estimations of calcium in sea water included the strontium. Miyake (1939) gives a value of 0·00075 for the ratio.

Sea water is not saturated with respect to strontium carbonate, the presence of neutral salts in water greatly increasing its solubility (Wattenberg, 1937).

The skeleton of a radiolarian, *Podocanalus*, is stated to be composed of strontium.

Sulphate. Thompson, Johnson & Wirth (1931) have determined the ratio of sulphate to chlorinity in a number of samples collected at varying depths from each of the oceans, including waters from the Eastern Mediterranean and the Red Sea. Only very small deviations from the value 0·1395 were found. The low salinity waters of the Baltic were exceptional, having a mean ratio of 0·1414. Previous investigations by Thompson, Lang & Anderson (1927) had shown a variation in

the ratio in waters diluted by natural means, and in water from which ice had frozen out.

Boron. The boron in sea water exists as boric acid, the greater part being undissociated at the hydrogen-ion concentrations ordinarily met with. Its apparent dissociation constants in salt solutions have been investigated (p. 62). Marine plants are rich in boron, their ash being stated to contain 1% B_2O_3 (Wattenberg, 1938).

The ratio of boric acid to chlorinity has been determined as 0·00137 by Harding & Moberg (1933) and by Ingelsrud, Thompson & Zwicker (1938). Miyake (1939) reports an increase in this ratio with depth in Pacific waters, the value changing from 0·00136 to 0·00162.

Artificial Sea Water

It is frequently desired to make an artificial sea water from laboratory reagents. Several formulae have been in use, of which the following, due to Lyman & Fleming (1940), includes all the major constituents and yields a water of Cl = 19·00% and salinity 34·5:

NaCl	23·477 g.	KCl	0·664 g.	H_3BO_3	0·026 g.
$MgCl_2$	4·981	$NaHCO_3$	0·192	$SrCl_2$	0·024
Na_2SO_4	3·917	KBr	0·096	NaF	0·003
$CaCl_2$	1·102				

H_2O to 1000 g.

Allowance has to be made for water of crystallization in any of the salts used. After thorough aëration the *p*H should lie between 7·9 and 8·3.

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IV. THE MINOR CONSTITUENTS

In addition to the salts already mentioned, sea water is known to contain small quantities of many other elements. The sum of these probably does not exceed 0·025 % of the major constituents. They tend to fall into two groups: those whose quantity varies widely because they are absorbed and further utilized by plant organisms, and those which do not undergo such wide fluctuations in quantity. Many of the latter, however, are found in, or adsorbed on, marine organisms at very much greater concentrations than they occur in sea water, together with other elements, which have not yet been detected in sea water. Some of these trace elements have a known function in the organism: as copper, which occurs in haemocyanin, the respiratory pigment of many invertebrate animals, and vanadium, which plays a part in the respiratory mechanism of others. Many of the trace elements are readily adsorbed on living organisms; copper, silver, gold, radium and uranium are found in greater concentration in water rich in plankton.

The following list shows the trace elements in milligrams per cubic meter of water:

		mg. per m³
Fluorine	Thompson & Taylor, 1933	1400
	Miyake, 1939	1300
Aluminium	Thompson & Robinson, 1932	1900
	Haendler & Thompson, 1939	160–1800
Lithium	Thomas & Thompson, 1933	100
Iodine	Reith, 1930; Schultz, 1930	50
Barium	Goldschmidt, 1937	50
Rubidium	Wattenberg, 1938	20
Arsenic (as arsenite)	Atkins & Wilson, 1926, 1927	19
	Rakestraw & Lutz, 1933	7–24
Copper	Atkins, 1932	10
	Riley, 1937	5–11
	Noddack, 1940	4
Zinc	Atkins, 1936	<8
	Noddack, 1940	14
Lead	Boury, 1930	4
	Noddack, 1940	5
Selenium	Wattenberg, 1938	4
Tin	Noddack, 1940	3
Caesium	Wattenberg, 1938	*circa* 2
Uranium	Hernegger & Karlick, 1935	2·0–2·2
	Foyn, Karlick, Petterson & Rona, 1939	0·15–1·6

		mg. per m³
Manganese	Thompson & Wilson, 1935	1–10
	Noddack, 1940	3
Thorium	Foyn, Karlick, Petterson & Rona, 1939	< 0·5
Vanadium	Ernst & Hoermann, 1936	0·2–0·3
Molybdenum	Ernst & Hoermann, 1936	0·3–0·7
	Noddack, 1940	0·5
Gallium	Noddack, 1940	0·5
Cobalt	Noddack, 1940	0·1
Nickel	Ernst & Hoermann, 1936	0·1
	Noddack, 1940	0·5
Bismuth	Noddack, 1940	0·2
Cerium	Goldschmidt, 1937	0·4
Scandium	Goldschmidt, 1937	0·4
Lanthanum	Goldschmidt, 1937	0·3
Yttrium	Goldschmidt, 1937	0·3
Mercury	Goldschmidt, 1937	0·3
Silver	Haber, 1928	0·3
	Noddack, 1940	0·15
Gold	Haber, 1928	0·004
	Noddack, 1940	·008
Iron	In true solution, Cooper, 1937	$< 10^{-}$
Radium	Evans, Kip & Moberg, 1938	0·3 to 0·9 × 10^{-7}
	Devaputra, Thompson & Utterback, 1932	0·4 to 4·7 × 10^{-7}
	Foyn, Karlick, Petterson & Rona, 1939	0·7 × 10^{-7}
Carbon	As organic carbon, Krogh *et al.*	1200–2000
Silica		10–1250
	In Antarctic	10–7000
Nitrogen	As nitrate	1–600
	As nitrite	0·1–50
	As ammonium	> 5 to 50
	As organic nitrogen	30–200
Phosphorus	As orthophosphate	> 1 to 60
	As organic P	0–16

A number of other elements have been found concentrated in various species of marine organisms. Webb (1937) has identified cadmium, the presence of which has not yet been reported in sea water; Noddack and Noddack, 1940 have identified titanium, chromium, cadmium, thallium, germanium and antimony.

Beharrell (1942) quotes a spectrographic analysis of seaweed dried to one-eighth of its original wet weight. This product was found to contain:

	mg. per kilo		mg. per kilo		mg. per kilo		mg. per kilo
Co	0·2	V	1	Ag	0·5	La	10
Ni	10	Mo	1	Zr	3	Au	1–10
Sn	1	Ga	0·5	Zn	40	Th	
Pb	1	Cr	1	Cu	10	Sc	

Copper. The waters of the English Channel have been found to contain some 10 mg. of copper per cubic metre in solution (Atkins, 1932). Determinations have been made by Riley (1937) off the mouth of the Mississippi, where 15 to 25 mg. per m^3 occur in the upper low salinity layers; with increasing distance offshore less copper was found in the waters. At a position some 100 miles offshore the upper layers contained 5 mg. per m^3, while the deep water contained 10 to 11 mg. per m^3.

It is considered that the concentration of copper in the sea is kept low because it is readily adsorbed on, or possibly combines with, organisms and detritus. If sea water enriched with copper to the extent of 50 or 100 mg. per m^3 is shaken with plankton organisms and organic detritus, the concentration of copper in solution is materially reduced, or if shaken with marine mud. A marked reduction also occurs if such water is kept in contact with various insoluble organic acids, such as a film or suspension of vegetable oils containing free acid or of rosin. Then the copper taken up from solution in the water is found in combination; it is soluble in such solvents as carbon tetrachloride, which do not remove copper ions from solution in sea water.

Thus there may be two agencies which control the concentration of copper, and of other heavy metals, in the waters of the oceans—adsorption on surfaces and combination with large organic molecules to form insoluble salts or co-ordination compounds which are only very slightly dissociated. The concentration of heavy metals in solution on marine organisms is generally referred to as the result of adsorption rather than combination with proteins or lipoids. Riley (1939) has studied the copper and plankton concentration in lake waters, finding a relation which follows the 'Freudlich adsorption isotherm'. This indicates that copper ions are more concentrated in the immediate vicinity of surfaces of organic matter, where, in addition, combination may take place.

The solubility of copper ions (cuprous are soon oxidized to cupric) in sea water is limited by the solubility of the green oxychloride which is precipitated and gradually changes to basic carbonate, the latter having a more blue-green colour. The solubility of this precipitate in sea water of *p*H 8 lies in the region of 180 mg. per m^3 and is much greater at *p*H values

below 7. When metallic copper is placed in sea water, cuprous ions are discharged; these are rapidly oxidized to cupric and heavy supersaturation results, which may persist long enough for concentration of 2000 mg. per m^3 of cupric copper to be temporarily attained.

Copper occurs in haemocyanin, the respiratory pigment of many marine invertebrate animals.

The addition of small quantities of copper to sea water is stated to have a remarkable effect on the free-swimming larvae of *Ostrea virginica*, causing them to settle almost immediately and metamorphose into the adult form.

The concentration of cupric ions, which is poisonous to marine plants and animals, varies around 1000 mg. per m^3, being different for different species—concentrations which are considerably above the ultimate saturation value at *p*H 8.

Iron. A variable quantity of iron occurs in sea water; from less than 1 to 50 or 60 mg. Fe per m^3 have been found in offshore waters. Part is retained by fine texture filter paper and all detectable traces, or almost all, by a membrane filter. Part is soluble in dilute acid and a further quantity is dissolved on heating with acid and an oxidizing agent such as bromine water.

The quantity in true solution is extremely small, owing to the insolubility of ferric hydroxide, while the quantity of ferrous ions which can remain in solution is limited by the oxidation-reduction potential of sea water which has been investigated (Cooper, 1937*b*). From solubility products and activities of ferrous, ferric and $FeOH''$ ions, Cooper (1937*a*) has concluded that sea water, when equilibrium has been attained, can contain no more than 4×10^{-7} and 3×10^{-8} mg. per m^3 as ionic iron in true solution at *p*H 8 and 8·5 respectively. In addition to this there may be traces of iron in solution in forms such as haem compounds set free in the breakdown of organisms. Such stable organic iron compounds have not been found in the sea; most organic compounds containing iron are slowly hydrolysed in sea water.

Estimations of iron in offshore waters have been made, notably by Braarud & Klem (1931) off the Norwegian coast, where 3 to 21 mg. Fe per m^3 were found, by Cooper (1935) in

the English Channel, who found similar quantities, while Thompson & Bremner (1935) found larger quantities ranging from 15 to 50 mg. per m^3 in the Pacific. At one position in the Atlantic Seiwell (1935) found no iron in the upper 40 metre layer by a method which would detect 1 to 2 mg. per m^3.

A seasonal change in the iron of the inshore waters of Puget Sound has been recorded by Thompson & Bremner, and a reduction in quantity after the spring growth of diatoms in the English Channel is recorded by Cooper. Various analyses of these plants yielded more iron than phosphorus, which points to the diatoms collecting all the iron in the water more than once during the course of a year. This implication lends particular interest to the nature of the iron present in the sea, since there is insufficient in true solution as iron ions to supply the plant with anything approaching the large quantities found when they were analysed.

It has been found that marine plant organisms can utilize insoluble ferric hydroxide, and that colloidal micelles or larger aggregates are readily adsorbed on their surface (Allen & Nelson, 1910; Harvey, 1937*a*). It is assumed that slow solution takes place at the interfacial layer, which is a seat of strong electrochemical forces and behaves as if it had a greater hydrogen-ion concentration than the surrounding water. Slow solution of adherent particles may then supply sufficient diffusible ionic iron for the intracellular requirements of the organism. Stable organic compounds, as haematin or haemoglobin, are not utilized by the plants. These observations, and also direct experiment, indicate that in nature plant organisms collect colloidal and larger aggregates of ferric hydroxide by adsorption.

The possibility that colloidal and larger aggregates of ferric phosphate, as well as of the hydroxide, occur in the sea is suggested by the observation that when sea water is shaken with ferric hydroxide its phosphate content is reduced to a low value, about 3 mg. P per m^3.

With regard to the presence of colloidal micelles of the hydroxide in sea water, direct experiment has shown that the rate at which they aggregate falls off materially at the very low concentrations which are likely to occur in the sea. Furthermore, they are afforded a considerable measure of protection against aggregation by the presence of almost equally low concentrations

of many organic substances, particularly by large molecules containing many hydroxyl groups.

When aggregation takes place with the formation of flocs, these sediment more or less rapidly. In the open ocean, beyond the influence of land drainage and where the upper layers are less dense than the water below, sedimentation may leave these upper layers almost iron free if turbulence (vertical mixing) is insufficient to keep them supplied with particles from below. The data obtained by Seiwell support this expectation.

The renewal of colloidal micelles or small aggregates is also likely to proceed through the iron collected by plant organisms being eaten with the plants and partly dissolved during digestion. When voided, the ferric hydroxide formed on mixing with the alkaline sea water will be in proximity to much protective colloid excreted at the same time.

The *determination of iron* in sea water by means of thiocyanate is detailed in the papers by Thompson & Bremner, Seiwell, Braarud & Klem. A method based on the red and violet association compounds formed by ferrous iron with 2 : 2′ dipyridyl and 2 : 2′ : 2″ tripyridyl has been used by Cooper (1935). With the former reagent quantities of iron in sea water down to less than 2 mg. Fe per m^3 could be ascertained; colour comparison was made between a 35 cm. column of the water and similar depths of standard solutions of an iron salt in distilled water. With the latter reagent less than 1 mg. Fe per m^3 could be detected.

For the estimation of the iron, readily soluble in acid, the following method was employed. To 100 c.c. of sea water, or standard solution of iron, were added four drops of 4 *N* hydrochloric acid and 1 c.c. of 10% sodium sulphite, and after 20 minutes, 1 c.c. of a solution containing 1% of di- or tripyridyl in 0·2 *N* hydrochloric acid. Colour comparisons were made 24 hours later. The salts present in sea water, other than iron, had no effect on the colour produced.

In order to estimate the total iron, preliminary boiling with acid and bromine water was employed.

Evidence relating to the utilization of iron by marine plants and the effect of scarcity upon their growth is presented on p. 136.

Manganese. Thompson & Wilson (1935) find 1 to 10 mg.

of manganese per cubic metre in solution in waters from the Pacific, and from 0·06 to 0·25 % of manganese in bottom muds off the American coast. They found the ash of plankton, mostly plant organisms, contained 0·07 % of manganese. A very small ratio of manganese to phosphorus in marine plankton from the English Channel was found by Cooper (1935). The possibility that lack of manganese may limit plant growth in some ocean areas is discussed on p. 139.

Radium. Variations in the radium content of sea water are recorded. Evans, Kip & Moberg (1938) find an increase in quantity with depth; in the Pacific, *circa* $0{\cdot}3 \times 10^{-7}$ mg. per m^3 were found at the surface and $0{\cdot}9 \times 10^{-7}$ at 900 metres. The radium content of marine plants and animals was found to be some 100 times greater than that of the water in which they live, and fine mud particles from bottom deposits in deep water were relatively rich in radium.

Devaputra, Thompson & Utterback (1932) find values of total radioactivity expressed in terms of radium ranging from 0·4 to $4{\cdot}7 \times 10^{-7}$ mg. per m^3 in waters from the Pacific and Atlantic, a small increase with increasing depth being usual.

Silica. Silica occurs in sea water as silicate, probably in true rather than colloidal solution, and is found in concentrations which vary widely. In the upper layers, where it has been utilized by diatoms, less than 20 mg. SiO_2 per m^3 is frequently found. At 3000 metres' depth off the west coast of Africa (Wattenberg, 1937*b*) 1400 mg. SiO_2 per m^3 and at the same depth in the Bay of Biscay (Atkins & Harvey, 1926) some 1200 mg. have been found. Clowes (1938) records high values, up to 7000 mg. SiO_2 per m^3, in the Antarctic deep water, and high values have also been recorded in the Pacific.

The seasonal changes in silicate content of the water of the English Channel have been observed by Atkins (1923–30) and by Cooper (1933). Concentrations of 200 to 400 mg. SiO_2 per m^3 were found in winter, falling in the spring to values as low as 10 mg. per m^3 in the upper layer. Marked fluctuations occurred during the summer, of greater amplitude than fluctuations in the phosphate or nitrogen salts. These suggest that the siliceous frustules of diatoms are rather soon redissolved after the plants have been eaten. More silicate was found near the bottom than in the layers immediately above.

Estimations of silica in sea water have been made from the yellow colour developed with molybdate in acid solution, the intensity of which bears a linear relation to the silicate, but is reduced by neutral salts in solution in the water (Atkins, 1923). The method, whose development has probably not yet reached finality, is reviewed by Wattenberg (1937*a*).

Estimation of silica. Two c.c. of a 10 % solution of ammonium molybdate are added to 100 c.c. of sea water, followed by the addition of four drops of 50 % sulphuric acid. The yellow colour develops within 10 minutes and remains constant for many hours. The effect of temperature and of considerable deviations from the quantities of added molybdate or acid are negligible.

The colour which develops can be matched against solutions of potassium chromate or of (pure) picric acid (11·35 mg. K_2CrO_4 or 1·09 mg. picric acid give an intensity of colour similar to that given by 1 mg. of Si, as silicate dissolved in distilled water).

The salts in sea water have a marked effect upon the colour developed by silicate in sea water.

Influence of salinity on colour intensity

Salinity °/₀₀	Brujewicz & Blinov Sea water	Wattenberg & Meyer	
		Sea water	NaCl solution
0	100	100	100
5	90	95	98
10	83	92	96
20	72	85	94
35	60	74	90

Wattenberg (1937*a*)

Organic Carbon Compounds

There is a small quantity of dissolved organic matter in sea water, variable in amount and derived from the excreta of living organisms and from solution of their tissues when dead. A small amount may leach from living plants, but it is doubtful if this occurs to any material extent before the plants die (Krogh, Lange & Smith, 1930).

The large amount of sodium chloride present makes estimation difficult. Krogh & Keys (1934) have developed a method of

direct combustion. A preliminary report of results obtained in this way (Keys, Christensen & Krogh, 1935) states that the organic matter in sea water is generally around 1·2 to 2 mg. carbon per litre with *circa* 0·2 mg. of organic nitrogen. This dissolved organic matter contains a small amount of phosphorus, and there are grounds for the inference that traces of organic sulphur compounds are also present.

The *organic nitrogen* in sea water has been estimated in the Atlantic by Von Brand & Rakestraw (1941), who found between 0·105 and 0·239 mg. N per litre, varying irregularly with depth. The samples had been stored for considerable periods. In the Pacific Robinson & Wirth (1934) found smaller quantities varying from 0·03 to 0·12 mg. N per litre. In inshore waters the quantities ranged up to 0·3 mg. N per litre. Much of the organic nitrogen is oxidized, yielding ammonia, when sea water is distilled with alkaline permanganate.

The *organic phosphorus* in the water at a position in the North Atlantic has been found by Redfield, Smith & Ketchum (1937) to vary from nil to 0·016 mg. P per litre, the greatest quantities occurring in the upper layers during summer and autumn.

A part of the organic matter in solution is readily broken down by bacteria. Various observations (p. 104) indicate that from 25 to 50 % is utilized when sea water is stored. The oxygen used and the carbon dioxide set free from waters collected from various localities due to bacterial activity during storage have been investigated, and also the oxygen consumed on treatment with permanganate. These various observations indicate more organic matter in solution in inshore than in offshore waters, and more during the summer than in winter.

The nature of the organic compounds in sea water has not been investigated. However, in the fresh water of Lake Mendota the total organic matter in solution ranges around 12 mg. per litre, about two to three times as much as in offshore sea water (Birge & Juday, 1934) and the total organic nitrogen ranges around 0·4 mg. per litre, also some two to three times more than in offshore sea water. In the lake water between 60 and 80 % of the organic nitrogen was in the amino-form and a quarter to a third precipitated by tannic and phosphotungstic acid. The water after freeing from organisms and evaporating gave positive

reactions for proteins. Estimations after hydrolysis showed an average of 13 mg. of tryptophane, tyrosine and histidine and of 4 mg. per cubic metre of cystine (Domogalla, Juday & Petterson, 1925; Petterson, Fred & Domogalla, 1925).

Salts containing Nitrogen and Phosphorus

The distribution and seasonal changes in orthophosphate and in salts containing nitrogen have been the subject of much investigation. These constituents are absorbed by plant organisms and built up into their cell substance.

As a result of plant growth, the upper layers may be exhausted of these nutrient salts. In some areas less than 0·5 mg. phosphate-P per m^3 is found with a few milligrams per cubic metre of nitrogen in the form of ammonium, nitrites and nitrates. In other areas, the salts containing nitrogen appear to be almost completely exhausted, leaving a few milligrams of phosphate-P per cubic metre. Such exhaustion is found in low latitudes, and, during summer, in temperate and sometimes in Arctic seas. In the Antarctic an abundance of nutrient salts are present in the upper layers throughout the summer, mixing due to turbulence being sufficient to keep the layers refreshed with water from beneath.

Below the photosynthetic zone, the concentration of phosphate and nitrogenous salts increases. The water below 100–150 metres contains a rich store of these nutrients.

The distribution of phosphate- and nitrogen-containing salts, also their estimation in sea water, are discussed on pp. 75–94: the regeneration of these salts from organisms on pp. 117–23; the effect of short supply of these salts on the rate of plant growth is discussed on pp. 133–35.

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V. DISSOLVED OXYGEN, ETC.

Dissolved Oxygen

The oxygen content of waters of varying salinity when saturated with air has been determined by Fox (1907) between 0° and 30° C., and is shown in Table 1.

In ordinary practice the oxygen in sea water is estimated by Winkler's method (Jacobsen & Knudsen, 1921). An accuracy of ±0·05 c.c. per litre is readily attainable if the titration is carried to a 'standard' pale lavender tint. The absolute value obtained by this method can be checked against the tabulated value for saturation in the following manner: a sea water of known salinity which has been stored in a bottle for several days is shaken with air and kept at constant temperature for several hours open to the air with occasional gentle agitation; the oxygen is then determined. The shaking tends to cause slight oversaturation, and final equilibrium is attained slowly. If the sample has not been stored for several days, rapid growth of bacteria is liable to absorb sufficient oxygen to vitiate the result.

Where only small quantities of water are available, as in some physiological experiments, a modification of this method, due to Krogh, gives an accuracy of 2%, using 1 to 2 c.c. of sea water (Fox & Wingfield, 1938).

The rate at which oxygen enters undersaturated water from the atmosphere has received attention. This rate shows a direct relation to the degree of undersaturation and is controlled by the rapidity with which the water at the air-water interface is renewed. Krogh (1910) measured the rate of solution of oxygen by water flowing past a small bubble of the gas. He observed that lower rates were found when using larger bubbles, and attributed this to incomplete renovation of the surface. Adeney (1928) has measured the rate of solution of oxygen from a bubble of air caused to travel up and down a tube filled with fresh and sea waters at various temperatures. Although deaerated fresh water absorbs oxygen more rapidly than sea

TABLE 1. *Number of c.c. of oxygen at N.T.P. dissolved in 1 litre of sea water saturated with air at the temperature shown and at 760 mm. pressure*

The chlorine content of the sea water is given in grams Cl per 1000 g. of sea water (Fox).

°C.	Cl=0	Cl=1	Cl=2	Cl=3	Cl=4	Cl=5	Cl=6	Cl=7	Cl=8	Cl=9	Cl=10	Cl=11	Cl=12	Cl=13	Cl=14	Cl=15	Cl=16	Cl=17	Cl=18	Cl=19	Cl=20
0	10·29	10·17	10·06	9 94	9·83	9·71	9·59	9·48	9·36	9 25	9·13	9·01	8·90	8·78	8·66	8·55	8·43	8·32	8·20	8·08	7·97
1	*10·02*	*9·90*	*9·79*	*9·68*	*9·57*	*9·45*	*9·34*	*9 23*	*9·12*	*9·01*	*8·89*	*8·78*	*8·67*	*8·56*	*8·44*	*8 33*	*8·22*	*8·11*	*8·00*	*7·88*	*7·77*
2	9·75	9·64	9·53	9·43	9 32	9·21	9·10	8·99	8·88	8·78	8·67	8·56	8·45	8·34	8·23	8·12	8·02	7·91	7·80	7·69	7·58
3	*9·50*	*9·39*	*9·29*	*9·19*	*9·08*	*8·98*	*8·87*	*8·77*	*8·66*	*8·56*	*8·45*	*8·35*	*8·24*	*8·14*	*8·03*	*7·93*	*7·82*	*7·72*	*7·61*	*7·51*	*7·40*
4	9·26	9·16	9·06	8·95	8·85	8·75	8·65	8·55	8·45	8·35	8·24	8·14	8·04	7·94	7·84	7·74	7·64	7·53	7·43	7·33	7·23
5	*9·03*	*8·93*	*8·83*	*8·73*	*8·64*	*8·54*	*8·44*	*8·34*	*8 24*	*8·14*	*8·05*	*7·95*	*7·85*	*7·75*	*7·65*	*7·56*	*7·46*	*7·36*	*7·26*	*7·16*	*7·07*
6	8·81	8·71	8·62	8·52	8·43	8·33	8·24	8·14	8·05	7·95	7·86	7·76	7·67	7·57	7·48	7·38	7·28	7·20	7·10	7·01	6·91
7	*8·60*	*8·50*	*8·41*	*8·32*	*8·23*	*8·14*	*8·04*	*7·95*	*7·85*	*7·77*	*7·68*	*7·59*	*7·50*	*7·40*	*7·31*	*7·22*	*7·13*	*7·04*	*6·95*	*6 85*	*6·76*
8	8·40	8·31	8·22	8·13	8·04	7·95	7·86	7·77	7·68	7·59	7·51	7·42	7·33	7 24	7·15	7·06	6·97	6·89	6·80	6·71	6·62
9	*8·21*	*8·12*	*8·03*	*7·95*	*7·86*	*7 77*	*7 69*	*7·60*	*7·52*	*7·43*	*7·34*	*7·26*	*7·17*	*7·09*	*7·00*	*6·91*	*6·83*	*6·74*	*6·66*	*6·57*	*6·48*
10	8·02	7·94	7·85	7·77	7·69	7·60	7·52	7 44	7·36	7·27	7·19	7·10	7 02	6·94	6·85	6·77	6·69	6·60	6·52	6·44	6·35
11	*7·84*	*7·76*	*7·68*	*7·60*	*7·52*	*7·44*	*7·36*	*7·28*	*7·20*	*7 12*	*7·04*	*6·96*	*6·88*	*6·80*	*6·71*	*6·63*	*6·55*	*6·47*	*6·39*	*6·31*	*6·23*
12	7·68	7·60	7·52	7·44	7·36	7·29	7·21	7·13	7·05	6 97	6·89	6 82	6·74	6·66	6·58	6 50	6·43	6·35	6·27	6·19	6·11
13	*7·52*	*7·44*	*7·36*	*7·29*	*7 21*	*7·14*	*7·06*	*6·98*	*6·91*	*6·83*	*6 76*	*6·68*	*6·61*	*6·53*	*6·46*	*6·38*	*6·31*	*6·23*	*6·15*	*6·08*	*6·00*
14	7·37	7·29	7·21	7 14	7·07	7·00	6·92	6·85	6·77	6 70	6·63	6·55	6 48	6·41	6 34	6·26	6·19	6·11	6·04	5·97	5·89
15	*7·22*	*7·15*	*7·07*	*7·00*	*6·93*	*6·86*	*6·79*	*6·72*	*6·64*	*6 57*	*6·50*	*6·43*	*6·36*	*6·29*	*6·22*	*6·14*	*6·07*	*6·00*	*5·93*	*5·86*	*5·79*
16	7·08	7·01	6·94	6·87	6·80	6·73	6·66	6·59	6·52	6 45	6·38	6·31	6·24	6·17	6·10	6·03	5·96	5 89	5·82	5·76	5·69
17	*6·94*	*6·88*	*6·81*	*6·74*	*6·67*	*6·60*	*6·54*	*6·47*	*6·40*	*6·33*	*6 26*	*6·20*	*6·13*	*6·06*	*5·99*	*5·93*	*5·86*	*5·79*	*5·72*	*5·66*	*5·59*
18	6·81	6·75	6·68	6·62	6·55	6·48	6·42	6 35	6 28	6 22	6·15	6·09	6·02	5·96	5·89	5·83	5·76	5·69	5·63	5 56	5·49
19	*6·69*	*6·63*	*6 56*	*6·50*	*6·44*	*6·37*	*6·30*	*6·24*	*6·17*	*6 11*	*6·05*	*5·98*	*5·92*	*5·86*	*5 79*	*5·73*	*5·66*	*5·60*	*5·53*	*5·47*	*5·40*
20	6·57	6·51	6·44	6·38	6·33	6·26	6·19	6·13	6·07	6·00	5 95	5·88	5·82	5·76	5·69	5·63	5·56	5·50	5·44	5·38	5·31
21	*6·46*	*6·40*	*6·33*	*6·27*	*6·22*	*6·15*	*6·09*	*6·03*	*5·96*	*5·90*	*5·85*	*5·78*	*5·72*	*5·66*	*5·59*	*5·53*	*5·47*	*5·41*	*5·35*	*5·29*	*5·22*
22	6·35	6·29	6·23	6 17	6·11	6·04	5 98	5·92	5·86	5 80	5·75	5 68	5·62	5·56	5·50	5 44	5·38	5·32	5·26	5·20	5·13
23	*6·24*	*6·18*	*6·12*	*6·06*	*6·01*	*5·94*	*5·88*	*5·82*	*5·77*	*5·71*	*5·65*	*5·59*	*5·53*	*5·47*	*5·41*	*5·35*	*5·29*	*5·23*	*5·17*	*5·11*	*5·04*
24	6·14	6·08	6·02	5·97	5·91	5·84	5·79	5·73	5·67	5·61	5·55	5·50	5·44	5·38	5 32	5·26	5·20	5·14	5·09	5·03	4·95
25	*6·04*	*5·99*	*5·92*	*5·87*	*5·81*	*5·75*	*5·69*	*5·64*	*5·58*	*5·52*	*5·46*	*5·41*	*5·35*	*5·29*	*5·23*	*5·17*	*5·12*	*5·06*	*5·00*	*4·95*	*4·86*
26	5·94	5·89	5·82	5·77	5·71	5·66	5·60	5·55	5·49	5·43	5·37	5·32	5·26	5·20	5·14	5·09	5·03	4·97	4·92	4·86	4·78
27	*5·84*	*5·79*	*5·73*	*5·67*	*5·62*	*5·57*	*5·51*	*5·46*	*5·40*	*5·34*	*5·28*	*5·23*	*5·17*	*5·11*	*5·06*	*5·00*	*4·94*	*4·89*	*4·83*	*4·78*	*4·70*
28	5·75	5·69	5·64	5·58	5·53	5·48	5·42	5·37	5 31	5·25	5·19	5·14	5·08	5·02	4·97	4·91	4·86	4·80	4·75	4·69	4·62
29	*5·66*	*5·60*	*5·55*	*5·49*	*5·44*	*5·39*	*5·33*	*5·28*	*5·22*	*5·16*	*5·10*	*5·05*	*4·99*	*4·93*	*4·88*	*4·83*	*4·77*	*4·71*	*4·66*	*4·60*	*4·54*
30	5·57	5·51	5·46	5 40	5·35	5·30	5·24	5·19	5·13	5·07	5·01	4·96	4·90	4·85	4·79	4·74	4·68	4·63	4·58	4·52	4·46

water, it required the same time for either to attain the same percentage saturation.

A relation between time, percentage saturation and temperature has been derived (Adeney, p. 68) from the data obtained by this method. From this, the rate of invasion of oxygen from air is deduced:

$$\text{Oxygen in c.c. entering 1 square cm. per minute} = 9{\cdot}6\ (t^\circ + 36)\ (a - x)\ 10^{-6},$$

where t° is the temperature of the water, x c.c. per litre is the concentration of oxygen present in the water, a c.c. per litre is the concentration of oxygen in the water at the temperature and salinity in question when saturated with air (Table 1).

The rates found under these conditions of surface renovation are considered by Adeney to represent maximum values likely to occur under natural conditions, and to be about twice the average rates occurring under open sea conditions.

The renovation of the surface, and consequently the rate of invasion, depends upon the extent to which the surface water is stirred by the wind. It is increased when the air is dry. Evaporation causes cooling at the surface and sets up convection currents which renovate the surface. This effect was found to be enhanced by increasing salinity up to about 15 $S^\circ/_{oo}$, evaporation causing an increase in density by concentration of the salts in addition to the increase in density caused by cooling.

Under quiescent conditions, as when deaerated water is exposed to the air in a vessel in the laboratory, the rate of invasion of oxygen may be more than one hundred times less than when the water is kept moving and the surface renovated. Under quiescent conditions the moisture content of the air plays a major part in controlling the rate of invasion.

The rate of liberation of oxygen from supersaturated water does not appear to have been investigated. During the period between minimum and maximum temperature at a position in the English Channel, Cooper (1933) has calculated that some 15 c.c. of oxygen are lost to the atmosphere per square cm.; of this amount, two-thirds were produced by phytoplankton organisms during photosynthesis, and the remaining third represented the

lesser quantity required to saturate the water at the higher temperature.

The distribution of dissolved oxygen in the oceans has been extensively investigated. The concentration depends upon the water's past history; upon when it was in contact with the air and upon the subsequent biological activity which has taken place in it, excess of respiration over photosynthesis lowering the concentration.

The surface waters are found to be close to the saturation value; the distribution of oxygen content follows the distribution of temperature and shows a similar seasonal variation. The concentration varies from some 8 c.c. O_2 per litre in the Arctic to 4·5 c.c. in the tropic surface waters. Slight supersaturation is frequently found, due to photosynthesis by plants in the upper layers; thus Deacon (1933) records 10 % supersaturation off the coast of South Georgia, Sverdrup (1933) 12 % in the Arctic and Cooper (1933) 8 % in the English Channel during the season of rapid phytoplankton growth. In the Antarctic undersaturated water has been found at the surface, due to oxygen-poor water welling up from below (Deacon, 1933).

A detectable diurnal variation has been observed in the surface layers of the Mediterranean and Atlantic, an increase in oxygen taking place during the day, due to photosynthesis by phytoplankton (Jacobsen, 1912). Close inshore and in estuaries with a rich flora of seaweeds a well-marked diurnal variation has been observed during the summer.

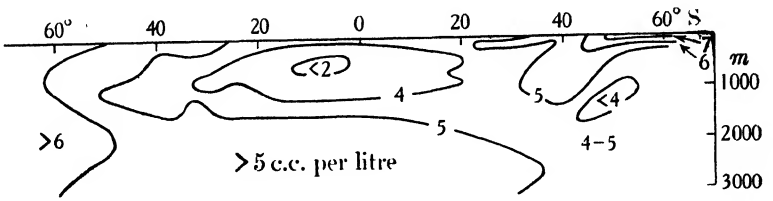

Fig. 13. Distribution of oxygen with depth in the waters of the Western basin of the Atlantic.

In deep ocean areas, the oxygen content diminishes below the photosynthetic layer in temperate and tropic seas, a minimum concentration occurring at 200 to 1000 metres' depth. Below

this the concentration rises and remains fairly constant below 1500 metres (Figs. 13 and 14).

The reduced concentration in the oxygen-poor layer is due, in part at least, to consumption of oxygen during the oxidation of falling particles of organic matter, coupled with slow renewal through eddy conductivity from the surface layers and from the deep water below. Minimum values are found in the most stable part of the water column, where the density of the water is increasing most rapidly with depth. With increasing density the fall of particles is slowed; moreover, the size of the particles decreases rather rapidly with time. Laboratory experiments (Seiwell & Seiwell, 1938) showed that the sinking velocities of dead plankton organisms decreased to less than one-tenth of the initial velocity after 14 days' storage.

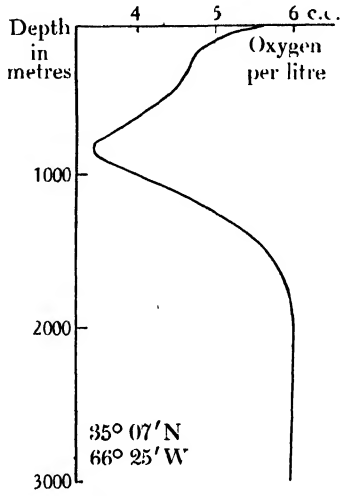

FIG. 14. Distribution of oxygen with depth in the subtropical north-west Atlantic. (After Seiwell.)

This rather simple explanation of oxygen shortage between depths of 600 to 800 metres in the tropical and subtropical Atlantic has been extended by Redfield (1942). He points out that the quantity of falling organic debris is not great in these relatively barren areas of the Atlantic, and that its oxidation is likely to be nearly completed before it has fallen as deep as the layer where least oxygen is found. In addition to depletion of oxygen by the debris of organisms falling from above, he includes the oxidation of organic debris which occurred in the water before it occupied its position in the 'oxygen-poor' layer of the tropics and subtropics, that is, when it was nearer the surface in higher and more fertile latitudes.

The oxygen-poor layer has been traced from 50° N. to 50° S. in the Atlantic. Wattenberg (1929) shows a sectional diagram from north to south through the eastern basin of the Atlantic,

with minima values as low as 1 c.c. O_2 per litre. In the western basin such low values are not found. Fig. 13, showing the distribution with depth in the western basin, is derived from sections by Seiwell (1934) and Deacon (1933).

A study of the oxygen distribution in this layer has led to some interesting tentative conclusions. It is considered, from its salinity and temperature, that the water north of about 15° or 20° N. originates from the Arctic and moves slowly southward below the upper layers, gradually losing oxygen en route; the water south of this originates from the Antarctic (40°–50° S.), moving slowly northward below the surface layers, as the Antarctic Intermediate Current. Seiwell (1934, 1937) has plotted the average oxygen content of the oxygen-poor layer between 1° and 32° N., and finds that the resulting curve drops to a minimum at about 15° N. and has the form of a regular series of undulations, the distance from peak to peak being about 200 miles. It is suggested that this periodicity arises as a result of the seasonal variation of phytoplankton growth, causing variations in oxygen content in those regions where the water masses were in the upper layers. These variations are considered to persist after the water has dipped down below the photosynthetic zone and moved great distances from the regions of origin. If this assumption is correct, it follows that the intermediate oxygen-poor layer moves at some 200 miles a year. Deacon (1933) has examined both the change in oxygen content and the change in salinity of the Antarctic Intermediate Current with change in latitude between 45° S. and 10° N., and obtained evidence of similar undulations.

A striking instance of the wealth of animal life in the oxygen-poor layer has been observed by Schmidt (1925) in the Gulf of Panama. Between 150 and 300 metres' depth the water was only 10 to 2 % saturated with oxygen. On the other side of the Panama isthmus, in the Caribbean Sea, the oxygen-poor layer between the same depths was 60 to 50 % saturated, yet in the low oxygen-content water in the Gulf of Panama a much larger amount of animal life was found between these depths.

In the deep water below about 1500 metres there is a gradual decrease in oxygen between the Arctic and Antarctic. This deep water is considered to be derived from water which falls from

the upper layers in high northern latitudes—in the Labrador Sea and between Iceland and Greenland. In this deep water there is also found slightly more oxygen in the western than in the eastern basins.

The oxygen content of the deep water of adjacent seas, cut off from the ocean circulation by submarine ridges, is of interest. In the Mediterranean the deep water is poorly oxygenated, while in the Black Sea the deep water is devoid of oxygen and hydrogen sulphide is present in quantity. Poor oxygenation is also found in the deep water of some fjords and in pockets in the Baltic.

Dissolved Nitrogen, etc.

The nitrogen in solution in sea water of varying salinity when in equilibrium with the air has been found and tabulated over a range of temperature by Fox (1907). It was noted by Rakestraw, Herrick & Urry (1939) that the sea was slightly undersaturated with nitrogen more frequently than might be expected when they based the saturation on the values given in these tables; this led them to suspect that slightly supersaturated waters had been used in Fox's determinations. It is notable that, when sea water is shaken with air, it becomes supersaturated, to the extent of about 2% after all bubbles have disappeared. Rakestraw & Emmel (1938) redetermined the solubility and obtained values slightly less than those previously found.

The solubility of both oxygen and nitrogen is affected similarly by changes in temperature and chlorinity. From the solubility values for oxygen (p. 44) the values for nitrogen may be calculated, from the relation

$$\text{c.c. } N_2 = \frac{\text{c.c. } O_2 + 0{\cdot}22}{0{\cdot}577},$$

within the range of 15–22°/$_{oo}$ chlorinity, where c.c. N denotes the volume of nitrogen, exclusive of inert gases, per litre, measured at N.T.P.

The *inert* gases, argon, etc., in solution are equal to about 2·7% of the dissolved nitrogen. From Rakestraw & Emmel's data the effect of change of temperature and chlorinity on their solubility differs from the effect on nitrogen. They have also found evidence

that traces of hydrogen or hydrocarbons occur in solution in inshore waters. The quantities of these inert gases in the sea appear to vary with the quantity of nitrogen in the water. Sea water also contains traces of helium and neon in solution; from 1·2 to $1{\cdot}8 \times 10^{-4}$ c.c. per litre of these gases were found by Rakestraw, Herrick & Urry (1939) in ocean waters from various depths.

The distribution of dissolved nitrogen in the oceans has received some attention, because the quantity in samples from various depths may give an indication of the temperature of the water when the water mass was in contact with the atmosphere.

It is considered to be a conservative constituent of the water, unaltered by biological changes. This is uncertain, since bacteria capable of forming nitrogen and bacteria capable of fixing atmospheric nitrogen are found in the sea (p. 112). However, the balance of evidence at present suggests that neither formation nor utilization takes place to any appreciable extent in the oceans.

The earlier data on nitrogen content have been reviewed by Buch (1929) and more recent data have been obtained by Rakestraw & Emmel at several deep-water positions in the Atlantic. The quantity of dissolved nitrogen found in the waters depended upon their temperature. It lay near the calculated requirement to saturate it, with respect to air, at the temperature of the water sample when brought to the surface. In the warmer upper layers supersaturation, up to about 8%, was frequently met with. In this connection it is of interest that if a saturated warm water is mixed with a saturated colder water, the resulting mixture will be supersaturated. Samples which were undersaturated, to a maximum extent of 5%, were also found. The bottom water, at 3000 to 4500 metres' depth, having a temperature of 3° to 2½° C., was within ± 4% of its saturation value, suggesting that it had not altered in temperature by more than 1½° C. since it had been in contact with the atmosphere at the surface in polar regions.

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VI. THE CARBON-DIOXIDE SYSTEM

SEA WATER contains carbon dioxide as bicarbonate and carbonate ions, as undissociated molecules of CO_2 and as carbonic acid, all in equilibrium with each other, and with the hydrogen ions present:

$$\begin{matrix} CO_2 \\ \uparrow\downarrow \\ H_2CO_3 \end{matrix} \rightleftharpoons HCO_3' + H^{\cdot} \rightleftharpoons CO_3'' + H^{\cdot}.$$

The water contains basic radicles in excess of the equivalent of strong acid radicles. This excess base is itself equivalent to the bicarbonate, carbonate and borate ions in the water. Other weak acids are present in such small quantities in water from the open sea that they do not come into the picture.

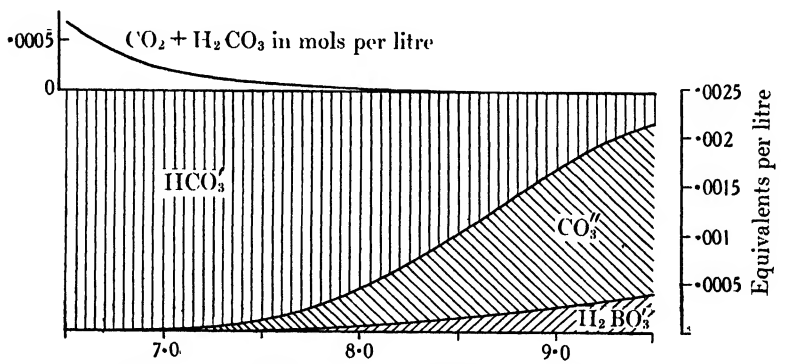

FIG. 15. Diagram showing change in constitution of an ocean water with changing *p*H. Temperature 16° C., salinity 36 °/₀₀, excess base 0·00246 equivalent per litre.

The diagram (Fig. 15) shows the change in these constituents with varying hydrogen-ion concentration for a typical ocean water of salinity 36 °/₀₀, at 16° C., containing 0·00246 equivalent of excess base per litre.

The free (unbound and undissociated) carbon dioxide consists of CO_2 and H_2CO_3 molecules in solution and in equilibrium with each other. The quantity of H_2CO_3 is about 1 % of the quantity of CO_2 molecules. This free carbon dioxide exerts a partial pressure. When sea water is shaken with a bubble of inert gas

for 5 to 10 minutes, carbon dioxide passes into the bubble, which will have attained a partial pressure of carbon dioxide equal to that exerted by the water. The carbon dioxide in the ocean water shown in the diagram would exert a partial pressure

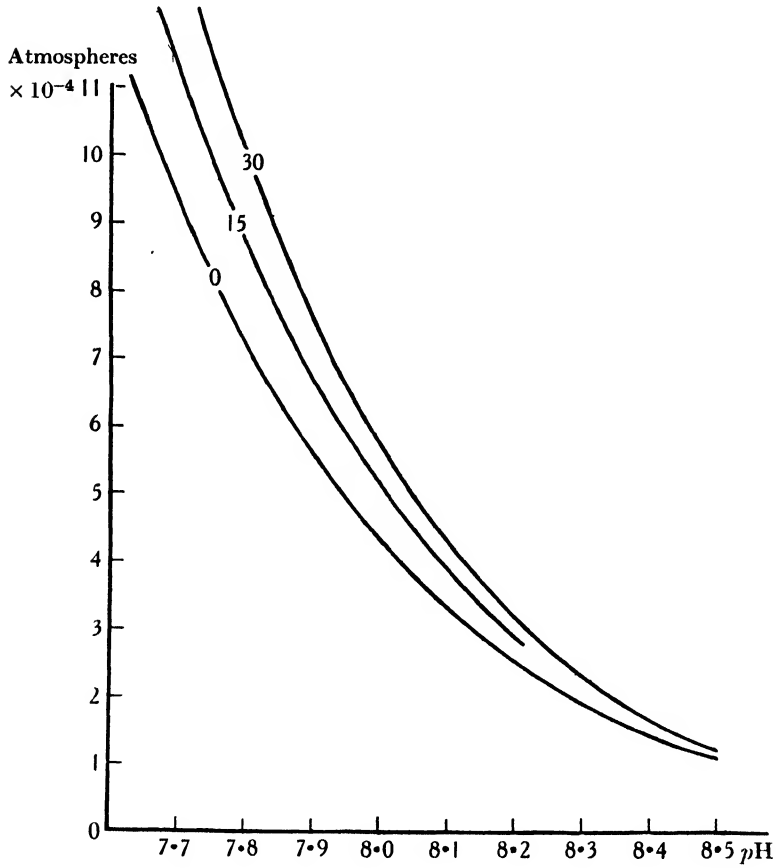

FIG. 16. The partial pressure of carbon dioxide in an ocean water of 36 °/₀₀ salinity, containing 0·00246 equivalent of excess base per litre, at 0°, 15° and 30° C.

at 16° C. equal to that in the atmosphere over the sea when its hydrogen-ion concentration approximates to *p*H 8·17. Fig. 16 shows the relation between partial pressure, temperature and *p*H.

When the *p*H of a sea water rises at constant temperature, carbon dioxide is set free into the atmosphere, free carbon

dioxide in solution diminishes and bicarbonate ions change to carbonate. This occasions a decrease in bound carbon dioxide, since the carbonate ions are divalent. Furthermore, some of the excess base becomes 'bound' to borate ions which are set free from undissociated boric acid.

It is possible to calculate the total carbon-dioxide content, its partial pressure and the concentration of bicarbonate or carbonate ions for a sea water of known salinity, temperature, *p*H and excess base. If one of these variables is altered a new state of equilibrium within the water system is attained within a few minutes. Transference of carbon dioxide to or from the air, however, takes place relatively slowly.

Hydrogen-Ion Concentration

The hydrogen-ion concentration in the upper layers of the open oceans varies within rather narrow limits. Values as low as *p*H 8 are rarely met with and the upper limit rarely exceeds *p*H 8·3. In shallow waters and rock pools the range is greater;

Table 2. *Change in p*H *of sea water for rise of* 1° C. (*x*)

From Buch & Nynäs (1939).

*p*H	Cl ‰ = 10			Cl ‰ = 15		
	0°–20°	10°–20°	20°–30°	0°–20°	10°–20°	20°–30°
7·4	−·0087	−·0084	−·0069	−·0088	−·0087	−·0076
7·6	92	92	79	95	96	83
7·8	100	101	89	103	105	90
8·0	108	109	94	110	112	94
8·2	114	115	98	115	117	96
8·4	117	117	99	118	118	98
*p*H	Cl ‰ = 19·5			Cl ‰ = 21		
	0°–20°	10°–20°	20°–30°	0°–20°	10°–20°	20°–30°
7·4	−·0089	−·0087	−·0081	−·0092	−·0089	−·0079
7·6	95	95	91	97	98	88
7·8	104	104	98	106	108	93
8·0	110	109	102	112	114	96
8·2	114	112	103	116	116	98
8·4	116	114	104	118	119	100

Note. The table contains some irregular values.

plants utilize carbon dioxide and raise the *p*H while the respiration of organisms acts in the opposite direction. At great depths in the oceans the *p*H is lowered owing to the effect of pressure; in the South Atlantic Wattenberg (1933) records values between *p*H 8·1 and 7·9 *in situ*. Intermediate layers are found in some areas where the decomposition of organisms falling from above is taking place; off the west coast of South Africa values of *p*H 7·6 *in situ* are recorded in such a layer at 400 metres' depth.

The hydrogen-ion concentration of any sample of sea water depends primarily upon the concentration of carbon dioxide and of the neutral salts. It is influenced by both the temperature of the water and by great pressure.

The effect of temperature on the hydrogen-ion concentration of sea water. The hydrogen-ion concentration increases (*p*H falls) with rising temperature, the increase depending upon the *p*H and salinity of the water. Table 2 shows this relationship under conditions where there is no interchange of carbon dioxide with the atmosphere. The values, copied from the original publication, show some minor irregularities. The values (x) in this table allow solution of the following equation:

$$pH_{t_2} = pH_{t_1} + x\,(t_2 - t_1),$$

where pH_{t_2} is the *p*H of the water at t_2 and pH_{t_1} is the *p*H at t_1.

*The effect of pressure on the p*H *of sea water.* When sea water is subjected to pressure at great depths, the dissociation constants of carbon dioxide are altered and as a result the *p*H of the water is decreased (p. 71). From investigations of the change in these constants, the change in *p*H has been calculated (Buch & Gripenberg, 1932):

*p*H at atmospheric pressure	Δ*p*H for increase of 1000 metres in depth
7·5	−0·035
7·6	−0·031
7·7	−0·028
7·8	−0·025
7·9	−0·023
8·0	−0·022
8·1	−0·021
8·2	−0·020
8·3	−0·020

Measurement of hydrogen-ion concentration. The hydrogen-ion concentration of sea water has been measured directly by means of the quinhydrone electrode for *p*H values up to about *p*H 8; the use of a hydrogen electrode is restricted, since the stream of gas washes carbon dioxide out of the water, causing a gradual rise in *p*H. Above *p*H 8, measurements are made by comparison with buffer solutions whose *p*H has been determined by means of the hydrogen electrode and is known for the temperature at which the comparison is made. This comparison is effected either by means of indicators or by means of the glass electrode.

The hydrogen-ion concentration of sea water is commonly determined by means of indicators against buffer solutions, the colour comparison being made visually or with a spectrophotometer or a photoelectric colorimeter; either instrument is stated to give values within 0·01 to 0·02 *p*H. It is necessary to take into consideration the salt error of the indicator, and the effect of the temperature at which colour comparison is made both upon the buffer solution and upon the indicator.

The salt error has been investigated for the commonly used indicators, against Palitzsch borate-boric acid buffers. It is a minus value; the corrected *p*H of the sea water is less than that of the buffer having the same colour. McClendon's buffer solutions calibrated at 20° C. are designed to have the same salt effect as ocean waters upon the indicator and hence dispense with this correction. However, they have the disadvantage that salts crystallize out from the solutions at low temperatures.

Salt error of indicators

Salinity (‰)	5	10	15	20	25	30	35
Cresol red, Xylenol blue	−0·04	0·12	0·17	0·21	0·23	0·25	−0·26
Thymol blue	−0·04	0·11	0·16	0·19	0·21	0·22	−0·23
Phenol red	−0·06	0·15	0·21	0·24	0·26	0·28	−0·29

From Buch & Nynäs (1939).

The effect of temperature on Palitzsch borax-borate buffer mixtures has been calculated by Buch (1929). The temperature coefficients (y), being the change in *p*H of the buffer solution for a rise of 1° C., are shown in Table 3.

TABLE 3. *Palitzsch borax-borate buffer mixtures*

Borax solution: 19·108 g. $Na_2B_4O_7$, 10 H_2O per litre.
Boric acid solution: 12·404 g. boric acid + 2·925 g. NaCl per litre.

Borax solution (c.c.)	Boric solution (c.c.)	*p*H at 18°	Temperature coefficient (*y*)
6·0	4·0	8·69	−0·0058
5·5	4·5	8·60	−0·0054
5·0	5·0	8·51	−0·0050
4·5	5·5	8·41	−0·0048
4·0	6·0	8·31	−0·0045
3·5	6·5	8·20	−0·0042
3·0	7·0	8·08	−0·0039
2·5	7·5	7·94	−0·0037
2·3	7·7	7·88	−0·0035
2·0	8·0	7·78	−0·0033
1·5	8·5	7·60	−0·0030
1·0	9·0	7·36	−0·0026
0·6	9·4	7·09	−0·0022

It is usual to make the colour comparison when the sample of sea water and the buffer solutions are at the same temperature (t_1). Under these circumstances, where Palitzsch buffers are used, the corrected *p*H of the sea water at the temperature of observation = *p*H observed + $y\ (18° - t_1)$ + 'salt error', and

$$pH_{t_w} = pH \text{ observed} + x\ (t_w - t_1) + y\ (18 - t_1) + \text{'salt error'},$$

where pH_{t_w} is the *p*H of the sea water *in situ* at t_w° C., and x, y and 'salt error' are each minus quantities.

If the temperature of the water sample differs from that of the buffer at the time of comparison, the effect of temperature on the dissociation of the indicator has also to be taken into consideration.

The glass electrode is coming into increasing use for the measurement of hydrogen-ion concentration in sea water. The method is only comparative, because the 'asymmetry potential' of the electrode varies and this necessitates standardizing the apparatus against a buffer solution before and after making a series of determinations. A study of the glass electrode method of comparison against the indicator method has been made by Buch & Nynäs (1939), who considered the accuracy similar to that obtained by indicators using a photoelectric colorimeter for comparison—a method to which they are inclined to give

preference and whose accuracy they estimate at 0·01 to 0·02 *p*H units. There is no 'salt error' in estimations made with the glass electrode; the temperature coefficient of the buffer solution used for standardizing has to be taken into account; the temperature coefficient of sea water (Table 2) allows the *p*H *in situ* to be calculated from the *p*H at temperature of observation.

The Dissociation Constant (ionic product) of Water and the Hydroxyl-ion Concentration

The hydroxyl-ion concentration, C_{OH_1} in gram mols per litre equals K_w/C_H, where K_w is the (molal) dissociation constant or ionic product of water. This value changes with temperature and with the salt content of sea water.

Effect of temperature on the ionic product of pure water

$T°$ C.	K_w or $C_H \times C_{OH}$	pK_w or pH+pOH	
0	$0{\cdot}12 \times 10^{-14}$	14·92	Kohlrausch & Heydweiller
	0·14	14·85	Lorentz & Bohi
16	0·63	14·20	Michaelis
18	0·74	14·130	,,
20	0·86	14·065	,,
22	1·01	13·995	,,
24	1·19	13·925	,,

The ionic product of water in sodium-chloride solutions has been investigated by Bjerrum & Unmack (1929), and, from the relations found by them, Buch (1938) has interpolated values for sea water. The result indicates that the molal ionic product in ocean water is about 1·75 times the value in fresh water.

From these values, the neutral point of ocean water, where the concentration of hydroxyl ions equals that of hydrogen ions, lies at *p*H 7·33 at 0° C., at *p*H 6·98 at 16° C. and at *p*H 6·84 at 24° C.

Bjerrum & Unmack (1929) have also investigated the activity of hydroxyl ions in salt solutions. These results indicate that the activity coefficient f_{OH} in ocean water is *circa* 0·945.

Cooper (1937) has made computations for sea water using the thermodynamic dissociation product

$$K_w = \frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}},$$

where a stands for the activity of the respective ion or molecule

and $a_x = f_x c_x$, where f is the activity coefficient of x, and c_x its molar concentration.

The thermodynamic product for pure water, where a_{H_2O} is unity, has been determined by Harned and co-workers. In sea water the effect of salts is to change the activity of the undissociated water, and of the hydroxyl ions. The pH as measured electrometrically, either direct or via indicators, is in fact a measurement of the activity and is more correctly pa_H. The effect of salts in sea water on the activity of the undissociated water, a_{H_2O}, has been found from the lowering of its freezing point or its vapour pressure (p. 65).

Hence the (thermodynamic) ionic product $(a_H \times a_{OH})$ for sea water $= K_w a_{H_2O}$, where a_{H_2O} is the activity of the water molecules in the sea water.

$t°$ C.	Water $pa_H + pa_{OH}$	Sea water (Cl = 19 °/₀₀) $pa_H + pa_{OH}$
0	14·939	14·947
5	·731	·739
10	·533	·541
15	·345	·353
20	·167	·175
25	13·997	·005
30	·832	13·840

Excess Base, Specific Alkalinity and Carbonate Alkalinity

The excess base, 'alkali reserve' or 'titration alkalinity' is found by titrating sea water with a strong acid. Since the normality of a natural sea water rarely exceeds 0·0026 N, it is desirable to adhere to a particular technique in order to obtain strictly comparable values. The following method (Wattenberg, 1933, p. 139) is in general use. A stream of air, washed free from CO_2, is passed through 200 c.c. of the sample of sea water to which 10 c.c. of $N/20$ HCl has been added and the liquid heated to boiling, in order to drive off all the CO_2 set free. The hot liquid is then back titrated with $N/20$ barium hydroxide using a mixture of 3 parts of Brom cresol green and 2 parts of methyl red as indicator, which gives a sharp end point at pH 5. The value so obtained is expressed in equivalents per litre.

Gripenberg (1937) points out that titration to *p*H 5 rather than to neutrality gives values which are too high by a small systematic error, and recommends titration to an end point between *p*H 6 and 7. Moreover, the precipitate formed during titration with barium hydroxide has a slight effect on the indicator, for which reason titration with sodium hydroxide is advocated.

There is, in general, a linear relation between excess base and the total salt content of the water. With some exceptions, the following relation is a close approximation

$$\frac{\text{Excess base} \times 10^3}{\text{Cl } ‰} = 0{\cdot}123 \quad \text{(the specific alkalinity).}$$

At great depths, calcium carbonate is dissolved from the bottom deposits and the specific alkalinity of the water layer close to the bottom is greater. In some areas calcareous organisms absorb calcium from the water and the specific alkalinity of the upper layers is reduced.

Wattenberg (1933) has determined the specific alkalinity of the water at a number of positions in the Atlantic. Mean values at various depths are shown in the following table:

Depth	Specific alkalinity
0 metres	0·1209
50	0·1207
100	0·1204
200	0·1210
250	0·1210
1000	0·1225
2500	0·1225
Close to bottom at *circa* 2000 metres	0·1225
3000	0·1241
4000	0·1250
5000	0·1267

The relation

$$\text{Excess base (in equivalents per litre)} = 0{\cdot}000123 \text{ Cl } ‰$$

only holds for waters which fall into neither of the above categories. Furthermore, in low salinity Baltic waters Gripenberg (1937) has found marked variations in the ratio between excess base and calcium.

Since the only weak acids in sea water which are known to

be present in sufficient quantity to affect the equilibria are carbonic and boric

$$\text{Excess base} = C_{HCO_3'} + 2C_{CO_3''} + C_{H_2BO_3'} + (C_{OH'} - C_{H\cdot}),$$

where $C_{HCO_3'}$, etc. is the concentration of the ion in gram ions per litre.

The term 'Carbonate alkalinity' is used for that part of the excess base which is equivalent to the bicarbonate and carbonate ions:

$$\begin{aligned}\text{Carbonate alkalinity} &= C_{HCO_3'} + 2C_{CO_3''} \\ &= \text{Excess base} - C_{H_2BO_3'} - (C_{OH'} - C_{H\cdot}).\end{aligned}$$

It remains to find the value of $C_{H_2BO_3'}$.

For boric acid in pure water at infinite dilution

$$\frac{C_{H\cdot} \times C_{H_2BO_3'}}{C_{H_3BO_3}} = K_B,$$

the dissociation constant for boric acid. This constant increases with temperature. In sea water the equilibrium is affected by the salts present. A table has been drawn up by Buch (1933, p. 62) giving values of the 'apparent' dissociation constant, K'_B, for various temperatures and chloride contents. This table, as are the others of dissociation constants, is expressed in terms of pK'_B or $\log 1/K'_B$, as is customary.

Unfortunately the equations defining the carbon dioxide system in sea water do not all lend themselves to solution in terms of logarithms. If the pK values are to be used, accessory tables are needed. Hence for the present purposes the several tables of pK values have been transposed into terms of K. The apparent constant K'_B for boric acid is given in Table 4.

The boron content of sea water is found to bear a direct linear relation to the chloride present. The total boron $C_{\Sigma B}$, or $C_{H_2BO_3'} + C_{H_3BO_3}$, approximates to $2{\cdot}2 \times 10^{-5} \times \text{Cl}\ ^{\circ}/_{\circ\circ}$ mols per litre. Hence

$$\text{Carbonate alkalinity} = \text{Excess base} - \frac{K'_B \times C_{\Sigma B}}{C_{H\cdot} + K'_B} - (C_{OH'} - C_{H\cdot})$$

or

$$\textbf{Carbonate alk.} = \textbf{Excess base} - \frac{K'_B \times 2{\cdot}2 \times \text{Cl}\ ^{\circ}/_{\circ\circ} \times 10^{-5}}{C_{H\cdot} + K'_B} - (C_{OH'} - C_{H\cdot}) \textbf{ equivalents per litre.}$$

(Equation 1)

TABLE 4. *Apparent dissociation constant* K'_B *of boric acid in sea water*

Buch (1933).

Cl ‰	S ‰	0°	2°	4°	6°	8°	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30° C.
15	27·1	1·10	1·15	1·20	1·23	1·29	1·35	1·41	1·44	1·51	1·55	1·62	1·70	1·78	1·82	1·91	$1·95 \times 10^{-9}$
16	28·9	1·12	1·17	1·23	1·29	1·35	1·38	1·44	1·51	1·55	1·62	1·70	1·74	1·82	1·91	1·95	2·00
17	30·7	1·17	1·23	1·29	1·32	1·38	1·44	1·51	1·55	1·62	1·70	1·74	1·82	1·91	1·95	2·04	2·09
18	32·5	1·20	1·26	1·32	1·38	1·44	1·48	1·55	1·62	1·66	1·74	1·82	1·86	1·95	2·00	2·09	2·14
19	34·3	1·26	1·32	1·35	1·41	1·48	1·55	1·62	1·66	1·74	1·82	1·86	1·91	2·00	2·09	2·14	2·24
20	36·1	1·29	1·35	1·41	1·48	1·55	1·58	1·66	1·74	1·78	1·86	1·95	2·00	2·09	2·14	2·24	2·29
21	37·9	1·32	1·38	1·44	1·51	1·58	1·66	1·70	1·82	1·86	1·91	2·00	2·09	2·14	2·24	2·29	2·40
0	$K_B =$	0·40	0·42	0·44	0·46	0·48	0·50	0·52	0·54	0·56	0·58	0·60	0·63	0·65	0·67	0·69	$0·72 \times 10^{-9}$

Within the range of *p*H 5·5 to 8·5, the value of $C_{OH'} - C_{H'}$ is negligible.

Relations between Bicarbonate, Carbonate, Carbonic Acid and Hydrogen-ion Concentration

In pure water at great dilution, the first dissociation

$$H_2CO_3 \rightleftharpoons H' + HCO_3'$$

takes up an equilibrium where

$$\frac{C_{H'} \times C_{HCO_3'}}{C_{H_2CO_3}} = K_1 \quad \text{(the first dissociation constant)}$$

for the particular temperature under consideration. The second dissociation, $HCO_3' \rightleftharpoons H' + CO_3''$, takes up an equilibrium where

$$\frac{C_{H'} \times C_{CO_3''}}{C_{HCO_3'}} = K_2 \quad \text{(the second constant).}$$

In sea water the concentrations of these ions are material. Furthermore, the neutral salts in the water reduce the *activity* of the water and permit the formation of complexes. Then

$$K_1 = \frac{a_{H'} \times a_{HCO_3'}}{a_{H_2CO_3}} \quad \text{and} \quad K_2 = \frac{a_{H'} \times a_{CO_3''}}{a_{HCO_3'}},$$

where *a* stands for the activity of the respective ion or molecule.

For working purposes, 'Apparent' dissociation constants, K_1' and K_2', have been used, where

$$K_1' = \frac{a_{H'} \times C_{HCO_3'}}{a_{H_2CO_3}} \quad \text{and} \quad K_2' = \frac{a_{H'} \times C_{CO_3''}}{C_{HCO_3}}.$$

These two equations define the constants which are given in Tables 5 and 6.

The unbound carbon dioxide in solution consists of free CO_2 with a small proportion of undissociated H_2CO_3. The term $a_{H_2CO_3}$ (the activity of the undissociated carbonic acid) has been taken as equal to $a_{CO_2} \times a_{H_2O}$.

From the definition of the activity of a volatile dissolved substance

$$a_{CO_2} = P_{CO_2} \times \alpha_0,$$

where P_{CO_2} is the partial pressure of CO_2 in atmospheres and α_0

TABLE 5. *The first apparent dissociation constant of carbon dioxide in sea water, K_1'*

Buch, Harvey, Gripenberg & Wattenberg (1932).

Cl °/₀₀	0°	2°	4°	6°	8°	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30° C.
15	0·60	0·63	0·65	0·67	0·71	0·74	0·77	0·79	0·83	0·86	0·89	0·91	0·94	0·97	1·00	$1·02 \times 10^{-6}$
16	0·61	0·64	0·66	0·69	0·72	0·75	0·79	0·82	0·84	0·87	0·91	0·93	0·96	0·98	1·01	1·05
17	0·62	0·65	0·67	0·70	0·73	0·76	0·79	0·83	0·85	0·89	0·92	0·95	0·97	1·00	1·03	1·06
18	0·63	0·66	0·68	0·71	0·74	0·77	0·81	0·84	0·87	0·90	0·93	0·96	1·00	1·02	1·06	1·09
19	0·64	0·67	0·69	0·73	0·76	0·79	0·82	0·85	0·88	0·92	0·95	0·97	1·00	1·04	1·07	1·10
20	0·65	0·68	0·71	0·74	0·77	0·80	0·83	0·87	0·89	0·93	0·97	1·00	1·02	1·04	1·09	1·12
21	0·66	0·69	0·72	0·75	0·78	0·81	0·84	0·88	0·91	0·96	0·98	1·01	1·04	1·07	1·10	$1·13 \times 10^{-6}$

TABLE 6. *The second apparent dissociation constant of carbon dioxide in sea water, K_2'*

Buch (1933).

Cl °/₀₀	0°	2°	4°	6°	8°	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30° C.
15	0·50	0·54	0·56	0·60	0·63	0·66	0·71	0·74	0·78	0·81	0·87	0·91	0·95	1·00	1·05	$1·10 \times 10^{-9}$
16	0·52	0·55	0·59	0·62	0·66	0·69	0·73	0·78	0·81	0·85	0·90	0·95	1·00	1·05	1·10	1·15
17	0·54	0·57	0·60	0·64	0·68	0·72	0·76	0·79	0·83	0·90	0·93	0·98	1·02	1·07	1·12	1·17
18	0·55	0·59	0·63	0·66	0·71	0·74	0·78	0·81	0·87	0·91	0·96	1·00	1·07	1·12	1·17	1·23
19	0·58	0·62	0·65	0·69	0·72	0·76	0·80	0·85	0·90	0·93	0·98	1·05	1·10	1·15	1·20	1·26
20	0·59	0·63	0·66	0·71	0·74	0·78	0·83	0·87	0·91	0·96	1·02	1·07	1·12	1·17	1·23	1·29
21	0·60	0·64	0·68	0·72	0·76	0·79	0·85	0·90	0·93	0·98	1·05	1·10	1·15	1·20	1·26	1·32
0	0·021	0·022	0·023	0·024	0·026	0·027	0·029	0·031	0·032	0·034	0·035	0·038	0·040	0·042	0·044	$0·046 \times 10^{-9}$

its solubility in (pure) water in mols per litre at 1 atmosphere pressure, at the particular temperature under consideration (Table 8).

a_{H_2O} is unity for pure water and is depressed by the presence of salts in solution. For any particular sea water it equals the ratio of its vapour pressure to that of pure water. This ratio has been determined and found to follow the equation

$$\frac{\text{V.P.}_{\text{sea water}}}{\text{V.P.}_{\text{water}}} = 1 - 0{\cdot}000969 \text{ Cl } {}^{\circ}/_{\circ\circ}.$$

The value of a_{H_2O} may also be derived from the depression of the freezing point of sea water below that of pure water, $\Delta t°$, by means of the Lewis and Randall equation

$$\log_{10} a_{H_2O} = -0{\cdot}004211\Delta t - 0{\cdot}0000022\Delta t^2.$$

TABLE 7. *The activity of water in sea water of varying salinity*

$$a_{H_2O} = \frac{\text{V.P.}_{\text{sea water}}}{\text{V.P.}_{\text{fresh water}}}.$$

Cl $^{\circ}/_{\circ\circ}$	a_{H_2O}	Cl $^{\circ}/_{\circ\circ}$	a_{H_2O}
2	0·998	14	0·986
4	0·996	16	0·984
6	0·994	18	0·983
8	0·992	20	0·981
10	0·990	22	0·979

Hence

$$K_1' = \frac{a_{H\cdot} \times C_{HCO_3'}}{P_{CO_2} \times \alpha_0 \times a_{H_2O}}.$$

From the relation

Carbonate alkalinity $= C_{HCO_3'} + 2C_{CO_3''}$, and the definition of K_2',

$$P_{CO_2} = \frac{\text{'Carbonate alkalinity'} \times a_{H\cdot}}{K_1'\alpha_0\left(1 + \dfrac{2K_2'}{a_{H\cdot}}\right) a_{H_2O}} \text{ atmospheres.}$$

(Equation 2)

From the equation

$$\text{Total } CO_2 = C_{HCO_3'} + C_{CO_3''} + C_{CO_2} \text{ in solution,}$$

since $C_{CO_2} = \alpha_s P_{CO_2}$, where α_s is the concentration of CO_2 in mols per litre soluble at 1 atmosphere in sea water of the

TABLE 8. *Solubility of carbon dioxide at 1 atmosphere pressure in water and sodium chloride solutions. The concentration of carbon dioxide, x, in mols per litre, and of sodium chloride in grams per kilo*

Derived from data by Bohr (1899)

NaCl °/₀	−2	−1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14° C.
0 α_0 =	0·0849	·0804	·0770	·0739	·0712	·0686	·0662	·0640	·0619	·0598	·0576	·0556	·0536	·0518	·0502	·0486	·0472 α_0
2 α_2 =	·0840	·0796	·0762	·0732	·0705	·0679	·0655	·0633	·0613	·0592	·0570	·0550	·0531	·0514	·0497	·0482	·0468 α_2
4	·0832	·0789	·0755	·0726	·0698	·0673	·0649	·0628	·0606	·0586	·0565	·0545	·0526	·0509	·0493	·0478	·0464
6	·0824	·0781	·0748	·0718	·0691	·0666	·0643	·0621	·0601	·0581	·0560	·0540	·0522	·0504	·0488	·0473	·0459
8	·0816	·0774	·0740	·0712	·0685	·0660	·0636	·0615	·0595	·0575	·0554	·0535	·0517	·0500	·0484	·0469	·0455
10	·0808	·0766	·0733	·0705	·0678	·0654	·0630	·0609	·0589	·0569	·0549	·0530	·0512	·0496	·0480	·0465	·0451
12	·0799	·0759	·0726	·0698	·0672	·0647	·0624	·0603	·0583	·0564	·0544	·0525	·0508	·0491	·0475	·0461	·0447
14	·0791	·0751	·0719	·0691	·0665	·0641	·0618	·0597	·0577	·0558	·0538	·0520	·0503	·0486	·0471	·0457	·0443
16	·0783	·0744	·0712	·0685	·0658	·0634	·0612	·0592	·0571	0552	·0533	·0515	·0498	·0482	·0467	·0453	·0439
18	·0775	·0737	·0705	·0678	·0652	·0628	·0606	·0586	·0566	·0547	·0528	·0510	·0493	·0478	·0462	·0448	·0435
20	·0767	·0729	·0698	·0671	·0646	·0622	·0600	·0580	·0560	·0542	·0522	·0505	0489	·0473	·0458	·0444	·0431
22	·0760	·0722	·0691	·0665	·0639	·0616	·0594	·0574	·0555	·0536	·0518	·0500	·0484	·0468	·0454	·0440	·0427
24	·0752	·0715	·0685	·0658	·0633	·0610	·0588	·0568	·0549	·0531	·0512	·0496	·0480	·0464	·0450	·0436	·0423
26	·0744	·0708	·0678	·0652	·0627	·0604	·0582	·0562	·0544	·0526	·0507	·0491	·0475	·0460	·0446	·0433	·0420
28	·0736	·0701	·0671	·0645	·0621	·0597	·0576	·0557	·0538	·0521	·0502	·0486	·0471	·0456	·0442	·0428	·0416
30	·0729	·0694	·0664	·0639	·0614	·0592	·0570	·0552	·0533	·0515	·0497	·0482	·0466	·0451	·0437	·0424	·0412
32	·0721	·0687	·0658	·0633	·0608	·0586	·0565	·0546	·0527	·0510	·0492	·0477	·0462	·0447	·0433	·0420	·0408
34	·0713	·0680	·0651	·0626	·0602	·0580	·0559	·0540	·0522	·0505	·0487	·0472	·0457	·0443	·0429	·0416	·0404
36	·0706	·0673	·0645	·0620	·0596	·0574	·0553	·0535	·0517	·0500	·0482	·0468	·0453	·0439	·0425	·0413	·0400
38	·0699	·0666	·0638	·0614	·0590	·0568	·0548	·0530	·0512	·0495	·0478	·0463	0449	·0435	·0421	·0409	·0397
40	·0692	·0659	·0632	·0607	·0584	·0562	·0542	·0524	·0506	·0490	·0473	·0459	·0445	·0431	·0417	·0405	·0393

NaCl °/₀	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30° C.
0 α_0 =	0·0458	·0442	·0429	·0417	·0405	·0394	·0384	·0372	·0361	·0351	·0341	·0332	·0322	·0314	·0306	·0299 α_0
2 α_2 =	·0454	·0439	·0426	·0413	·0402	·0391	·0380	·0369	·0358	·0348	·0338	·0329	·0320	·0312	·0304	·0296 α_2
4	·0450	·0435	·0422	·0410	·0398	·0388	·0377	·0366	·0355	·0345	·0336	·0326	·0318	·0310	·0302	·0294
6	·0446	·0331	·0419	·0406	·0395	·0384	·0374	·0363	·0353	·0343	·0333	·0324	·0315	·0307	·0300	·0292
8	·0442	·0427	·0415	·0403	·0392	·0381	·0371	·0361	·0350	·0340	·0331	·0322	·0313	·0304	·0297	·0290
10	·0438	·0424	·0412	·0400	·0388	·0378	·0368	·0358	·0347	·0337	·0328	·0319	·0310	·0302	·0295	·0288
12	·0434	·0420	·0408	·0396	·0385	·0375	·0365	·0355	·0344	·0335	·0325	·0317	·0308	·0300	·0293	·0286
14	·0430	·0416	·0404	·0393	·0382	·0372	·0362	·0352	·0341	·0332	·0323	·0314	·0306	·0298	·0291	·0283
16	·0426	·0413	·0401	·0389	·0379	·0369	·0359	·0349	·0339	·0329	·0320	·0312	·0304	·0296	·0288	·0281
18	·0422	·0409	·0398	·0386	·0376	·0366	·0356	·0346	·0336	·0326	·0318	·0309	·0301	·0293	·0286	·0279
20	·0419	·0406	·0394	·0383	·0372	·0363	·0353	·0343	·0333	·0324	·0315	·0307	·0299	·0291	·0284	·0277
22	·0415	·0402	·0391	·0380	·0369	·0360	·0350	·0340	·0331	·0322	·0313	·0305	·0296	·0289	·0282	·0275
24	·0411	·0398	·0387	·0376	·0366	·0357	·0347	·0337	·0328	·0319	·0310	0302	·0294	·0287	·0280	·0273
26	·0407	·0395	·0384	·0373	·0363	·0354	·0345	·0335	·0325	·0316	·0308	·0300	·0292	·0284	·0278	·0271
28	·0403	·0391	·0380	·0370	·0360	·0351	·0341	·0332	·0323	·0314	·0305	·0297	·0290	·0282	·0275	·0269
30	·0400	·0388	·0377	·0366	·0357	·0348	·0339	·0329	·0320	·0311	·0303	0295	·0288	·0280	·0273	·0267
32	·0396	·0384	·0374	·0363	·0354	·0345	·0336	·0326	·0318	·0309	·0301	·0293	·0285	·0278	·0271	·0265
34	·0393	·0381	·0371	·0360	·0351	0342	·0333	·0323	·0315	·0306	·0298	·0290	·0283	·0276	·0269	·0263
36	·0389	·0377	·0367	·0357	·0348	·0339	·0330	·0321	·0312	·0304	·0295	·0288	·0281	·0273	·0267	·0261
38	·0385	·0374	·0364	·0354	·0345	·0336	·0327	·0318	·0309	0301	·0293	·0286	·0279	·0271	·0265	·0259
40	·0382	·0371	·0361	·0351	·0342	·0333	·0324	·0315	0307	·0299	0291	·0283	0276	0269	·0263	·0257

particular salinity and temperature under consideration (Table 8):

$$\text{Total } CO_2 = \frac{\text{'Carbonate alkalinity'}}{1+\frac{2K_2'}{a_{H\cdot}}} \times \left(1+\frac{K_2'}{a_{H\cdot}}+\frac{\alpha_s \times a_{H\cdot}}{K_1' \times \alpha_0 \times a_{H_2O}}\right) \text{ gram mols per litre.} \quad \text{(Equation 3)}$$

TABLE 9. *Table showing the relation between pQ and C_Q*

$$pQ = \log \frac{1}{Q}$$

pQ	C_Q	pQ	C_Q	pQ	C_Q
Q ·00	$1{\cdot}000 \times 10^{-Q}$	Q ·34	$0{\cdot}457 \times 10^{-Q}$	Q ·67	$0{\cdot}214 \times 10^{-Q}$
·01	·977	·35	·447	·68	·209
·02	·955	·36	·437	·69	·204
·03	·933	·37	·427	·70	·200
·04	·912	·38	·417	·71	·195
·05	·891	·39	·407	·72	·191
·06	·871	·40	·398	·73	·186
·07	·851	·41	·389	·74	·182
·08	·832	·42	·380	·75	·178
·09	·813	·43	·372	·76	·174
·10	·794	·44	·363	·77	·170
·11	·776	·45	·355	·78	·166
·12	·759	·46	·347	·79	·162
·13	·741	·47	·339	·80	·158
·14	·725	·48	·331	·81	·155
·15	·709	·49	·324	·82	·151
·16	·692	·50	·316	·83	·148
·17	·676	·51	·309	·84	·144
·18	·661	·52	·302	·85	·141
·19	·646	·53	·295	·86	·138
·20	·631	·54	·288	·87	·135
·21	·617	·55	·282	·88	·132
·22	·603	·56	·275	·89	·129
·23	·589	·57	·269	·90	·126
·24	·575	·58	·263	·91	·123
·25	·562	·59	·257	·92	·120
·26	·549	·60	·251	·93	·117
·27	·537	·61	·245	·94	·115
·28	·525	·62	·240	·95	·112
·29	·513	·63	·234	·96	·110
·30	·501	·64	·229	·97	·107
·31	·490	·65	·224	·98	·105
·32	·479	·66	·219	·99	·102
·33	·468				

From these three equations, the total CO_2 and the partial pressure of CO_2 can be calculated for a natural sea water, or for one to which a strong acid or base has been added. In the same way, the pH (in reality the $pa_{H^\cdot}$) can be calculated for a water to which acid or base has been added. Such calculated values agree within the limits of experimental error with those found.

From the definitions of carbonate alkalinity and of K_2' the following two equations are derived:

$$C_{CO_3''} = \frac{\text{Carbonate alkalinity} \times K_2'}{2K_2' + a_{H^\cdot}} \text{ gram ions per litre,} \qquad \text{(Equation 4)}$$

$$C_{HCO_3'} = \frac{\text{Carbonate alkalinity}}{1 + \frac{2K_2'}{a_{H^\cdot}}} \text{ gram ions per litre.} \qquad \text{(Equation 5)}$$

The following examples illustrate the use of these equations. A sea water having a salinity of 35·35 °/₀₀ (Cl °/₀₀ = 19·5) is found to have an excess base of 0·0024 equivalent per litre.

(*a*) What is the partial pressure of CO_2 which this water exerts when at 15° C. with a pH of 8·1?

From Table 9, when pH = 8·1, the concentration of fully active hydrogen ions is $0{\cdot}794 \times 10^{-8}$ gram ions per litre.

$$C_{H^\cdot} \text{ or } a_{H^\cdot} = 0{\cdot}794 \times 10^{-8}.$$

From Table 4, K_B' for water of 19·5 °/₀₀ Cl at 15° C. is $1{\cdot}73 \times 10^{-9}$.

From Equation 1,

$$\text{Carbonate alkalinity} = 0{\cdot}0024 - \frac{K_B' \times 42{\cdot}9 \times 10^{-5}}{0{\cdot}794 - 10^{-8} + K_B'} = 0{\cdot}0023.$$

From Tables 5 and 6,

$$K_1' = 0{\cdot}875 \times 10^{-6} \text{ and } K_2' = 0{\cdot}88 \times 10^{-9} \text{ at } 15° \text{ C.}$$

From Tables 8 and 7, $\alpha_0 = 0{\cdot}0458$ mols per litre and $a_{H_2O} = 0{\cdot}981$.

By substituting these values in Equation 2,

$$P_{CO_2} = 3{\cdot}82 \times 10^{-4} \text{ atmospheres.}$$

(*b*) What loss of carbon dioxide will cause the pH of this water to rise from 8·1 at 15° C. to 8·4 at 25° C.?

The carbonate alkalinity (0·0023 mols per litre) at 15° C. and *p*H 8·1 has been calculated. The value of α_s for a salt solution of similar salinity at this temperature is 0·0390 mol per litre (Table 8). The other constants for water of this salinity at 15° C. have already been taken from the tables. On substituting these in Equation 3 and resolving,

Total CO_2 at 15° C. and *p*H 8·1 = 0·00211 mol per litre.

At 25° C. and *p*H 8·4, $K'_B = 2{\cdot}07 \times 10^{-9}$ (Table 4) and $a_H = 0{\cdot}398 \times 10^{-8}$ (Table 9). From Equation 1,

Carbonate alkalinity at 25° C. and *p*H 8·4

$$= 0{\cdot}0024 - 0{\cdot}000146 = 0{\cdot}00225.$$

The other constants for water of this salinity at 25° C. are taken from the tables:

$$K'_1 = 1{\cdot}025 \times 10^{-6}, \qquad K'_2 = 1{\cdot}135 \times 10^{-9},$$
$$\alpha_0 = 0{\cdot}0341, \qquad \alpha_s = 0{\cdot}0295.$$

On substituting these values in Equation 3 and resolving,

Total CO_2 at 25° C. and *p*H 8·4 = 0·00185 mol per litre.

Hence loss of carbon dioxide is 0·00026 mol per litre.

(*c*) What *p*H will this water attain when in equilibrium at 15° C. with an inert gas containing 0·02 % CO_2?

The first of these examples showed that this water at *p*H 8·1 was in equilibrium with an atmosphere containing 0·0382 % CO_2. With gas containing less carbon dioxide the *p*H will be higher and the 'Carbonate alkalinity' will be reduced due to the formation of borate ions. By combining Equations 1 and 2, an equation is obtained from which the *p*H may be calculated for a partial pressure of 2×10^{-4} atmospheres, but the calculation is intractable. Reference to Fig. 16 indicates that the value will lie in the neighbourhood of *p*H 8·3. It is simpler to calculate the 'Carbonate alkalinity' for *p*H 8·3 and 8·5 from Equation 1, and with these values calculate the P_{CO_2} from Equation 2. After plotting the calculated values of the P_{CO_2} against *p*H for 8·1, 8·3 and 8·5, the *p*H for a partial pressure of 2×10^{-4} atmospheres can be read from the graph.

Experimental Determination of the Apparent Dissociation Constants

A brief description of the methods employed to determine the two carbon-dioxide dissociation constants makes clearer their meaning and their use.

The first apparent constant K_1' alone shows the relation between pH, bicarbonate ions and carbon dioxide in solution in sea water with a pH below about 7, when carbonate ions almost cease to exist. In order to determine this constant, sea water was shaken for about 10 minutes at constant temperature with air enriched with carbon dioxide, the air in contact with the sample of sea water being kept at atmospheric pressure. Equilibrium being attained, the partial pressure of CO_2 in the air in contact with the water, and hence in the water, was found by determining the carbon-dioxide content of this air manometrically. This provides P_{CO_2} in Equation 2. The pH ($pa_{H\cdot}$) of the water was determined with a quinhydrone electrode. The term $2K_2'/a_H$ in the equations becomes negligibly small with a pH below 7. Hence, having determined the excess base and calculated 'Carbonate alkalinity', K_1' can be found from the equation. From a number of such calculations for a particular sea water in equilibrium with air of varying CO_2 content, its K_1' was obtained. Similar determinations at other temperatures, and for waters of differing salinities, gave the variation of K_1' with temperature and salinity. In practice deductions were made from the observation of other workers concerning the effect of temperature and salt concentration on the dissociation of sodium bicarbonate solutions.

The practical determination of the second constant, K_2', presented greater difficulties. It was necessary to work at hydrogen-ion concentrations where carbonate ions formed a material proportion of the bound CO_2. Under these conditions, P_{CO_2} is very small and the experimental error in its determination affects the result. In order to overcome the first difficulty, the total CO_2 has been used. This is determined by boiling off the dissolved gases from the water sample under reduced pressure after adding phosphoric acid. The pH was measured colorimetrically in the earlier experiments (Buch, Harvey,

Gripenberg & Wattenberg, 1932; Moberg, Greenberg, Revelle & Allen, 1934) and later with a hydrogen electrode (Buch, 1938). The water in these experiments was brought to a *p*H where the carbonate exceeded the bicarbonate ions (*circa* *p*H 8·8) by aerating with carbon dioxide free air or with hydrogen, and in the latter experiments an artificial sea water without boric acid was used in order to omit this further complication. It is to be noted that in this relatively high range of *p*H, the excess of hydroxyl ions over hydrogen ions is material, and the last term in Equation 1 cannot be neglected.

Moberg *et al.* also employed a titration method for estimating the total carbon dioxide in the water. The quantity of strong acid required to bring a sea water to the turning point of phenolphthalein (at which point almost all the carbonate ions originally present have changed to bicarbonate ions and free carbon dioxide) was taken as strictly equivalent to the carbonate originally present. The effect of the borate ions was neglected. In waters of high *p*H, the quantity of acid required by the hydroxyl ions was subtracted. The equivalence of acid required was taken as equal to $C_{CO_3''}$ and the excess base as $C_{HCO_3'} + 2C_{CO_3''}$. The difference (that is $C_{HCO_3'} + C_{CO_3''}$) was taken as equal to the total CO_2, since the quantity of free CO_2 in solution above *p*H 8·1 is only a fraction of 1 % of the combined CO_2. The rough values for CO_2 obtained in this way lay within $3\frac{1}{2}$ ‰ of the values found by a manometric technique. The titration method is discussed by Greenberg, Moberg & Allen (1932).

The Effect of Pressure at Great Depths

With increase in pressure there is a change in the carbon-dioxide system. The two constants K_1' and K_2' both increase. The water is compressed; the pressure at 10,000 metres' depth causes a diminution of some 4 % in volume. In consequence both the 'excess base' and total carbon dioxide, which are expressed in terms of equivalents and gram mols per litre respectively, are increased.

As a result of pressure, the free unbound carbon dioxide in solution decreases, the bicarbonate increases and the hydrogen-ion concentration increases (p. 55) (Buch & Gripenberg, 1932).

The following table, from Buch & Gripenberg, shows the changes due to increasing depth for a water of Cl $^{o}/_{oo} = 19{\cdot}5$ at 0° C.:

Depth in metres	*p*H	Excess base	$C_{\Sigma CO_2}$	C_{CO_2}	$C_{HCO_3'}$	$C_{CO_3''}$
0	8·00	2·40	2·23	0·026	2·00	0·20
5,000	7·89	2·45	2·27	0·020	2·05	0·20
10,000	7·78	2·50	2·31	0·015	2·09	0·20
0	7·60	2·40	2·38	0·074	2·22	0·09
5,000	7·44	2·45	2·42	0·063	2·29	0·08
10,000	7·27	2·50	2·48	0·052	2·36	0·07

The effect of pressure on the first dissociation constant has been investigated by Brander. The effect on the second constant K_2' is considered to be the same as the effect of pressure on other weak acids; presumably K_B' is affected in the same way. The following values have been taken from the table compiled by Wattenberg (1933, p. 251):

Depth in metres	Percentage increase in K_2'	Percentage increase in K_2'
0		
2,000	26	9·6
4,000	58	20
6,000	100	32
10,000	202	55

Interchange of Carbon Dioxide between the Sea and the Atmosphere

Krogh determined the partial pressure of carbon dioxide in a series of samples from the surface between Scotland and Canada by shaking the water with a small bubble of air. After shaking, such a bubble will contain *circa* 0·03 % of CO_2, indicating a partial pressure of CO_2 amounting to 3×10^{-4} atmospheres. In general the partial pressure in the water was less than the partial pressure in the atmosphere. Hence it is absorbed from the air, the sea acting as a regulator of the carbon dioxide in the atmosphere.

Buch (1939 *a* and *b*) has made similar observations during summer months between Denmark and America and between

Norway and Iceland, finding that the partial pressure in the air over the North Atlantic during summer varied around $3{\cdot}1 \times 10^{-4}$ atmospheres, less over the Arctic and rather more over land. In one series of observations the partial pressure was found to increase with height above the sea surface. The partial pressure in the surface water was found experimentally and by calculation from *p*H, salinity and temperature. It varied, but on an average was some 5 % less than in the atmosphere. These series of observations confirmed Krogh's conclusions.

With regard to conditions during the winter months, Cooper (1933) has made observations of the surface water in the English Channel which indicate that the water exerts a greater partial pressure of carbon dioxide during the winter than during the summer. A marked decrease in partial pressure occurred between mid February and mid May during the period of maximum phytoplankton population, which utilized carbon dioxide and thereby increased the *p*H of the water.

Deacon (1940) gives data for the waters of the subtropical South Atlantic and of the Antarctic, which also show a greater partial pressure during the winter months.

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VII. THE DISTRIBUTION AND ESTIMATION OF PHOSPHATE AND OF SALTS CONTAINING NITROGEN

Distribution of Phosphate

The distribution of phosphate in the oceans has been extensively studied since 1923, when a rapid method of determination was developed by Atkins. This allows concentrations as low as 0·5 mg. phosphate-P per m^3 to be detected. It has been found that the salts in sea water affect the results (p. 80) and necessitate the application of a factor for salt error. In the following account of the distribution of phosphate, a factor of 1·35 has been applied to values recorded in the earlier literature.

In the Arctic, the phosphate in the surface layers is exhausted in some areas during the summer (Kreps & Verjbinskaya, 1932), in other areas reduced to low values (Böhnecke, Hentschel & Wattenberg, 1930; Böhnecke, Foyn & Wattenberg, 1932). Here, as elsewhere, exhaustion is due to turbulence bringing insufficient phosphate from the water below. The deep water of the Arctic contains *circa* 40 mg. phosphate-P per m^3

The surface water of the temperate North Atlantic undergoes a regular seasonal change in its phosphate content; during summer the concentration rarely exceeds 3 mg. P per m^3 (Seiwell, 1935). In the Gulf of Maine, observations by Bigelow, Lillick & Sears (1940) indicate that a few milligrams remain. They found more complete exhaustion of nitrate and nitrite, while Redfield & Keys (1938) found complete exhaustion of ammonium-nitrogen in the surface layers during summer. These observations suggest a slight surplus of phosphates over available nitrogen for the plants' requirements in this area.

The seasonal variation of phosphate at a position in the English Channel has been followed at monthly intervals for a number of years. From winter maximum values varying between 21·5 and 14·5 mg. P per m^3 it has fallen in some years to less than 0·5 in the upper layers, in other years 2 or 3 milligrams remain (Atkins, 1923–30; Cooper, 1933, 1938). The changes

which took place during 1924 are shown in Fig. 17. The fluctuations from year to year in the maximum concentration of phosphate found during the winter are discussed on p. 152. In the southern hemisphere, a similar seasonal variation has been found by Dakin & Colefax (1935, 1940).

The deep water of the temperate North Atlantic contains phosphate ranging from 34 to 48 mg. P per m^3 (Seiwell, 1935; Atkins & Harvey, 1926).

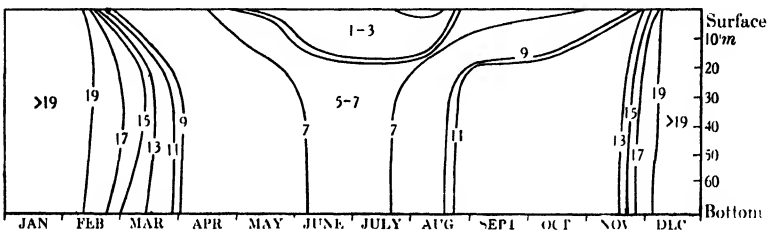

FIG. 17. Variation in phosphate during 1924 at a position in the English Channel. Numbers indicate milligrams of phosphate-phosphorus per cubic metre of water.

In the subtropical and tropical waters of the North Atlantic the upper layers remain depleted of phosphate throughout the year, except off the African coast, where the surface waters are replenished from below and 13 to 26 mg. P per m^3 is found over an extensive area. Here planktonic plants and animals are particularly abundant. The phosphate concentration increases rapidly with increasing depth below the photosynthetic zone. Over much of the area it reaches a maximum at some 750 to 1000 metres (Seiwell, 1935; Deacon, 1933; Wattenberg, 1933; Clowes, 1938; Rakestraw & Smith, 1937) with concentrations of 65 to 80 mg. phosphate-P per m^3. This 'zone of decay' which underlies the photosynthetic zone or productive layer is also marked by depleted oxygen content and the presence of nitrite. Below it, the deep water extending to a depth of 2 miles or more contains 40 to 47 mg. P per m^3.

On passing further south towards the Antarctic, increasing quantities of phosphate are found in the surface layers. Between 40° and 50° S. some 23 to 55 mg. P per m^3 are recorded. The deep water also becomes increasingly richer in phosphate, particularly in the western part of the South Atlantic, where 65 to 90 mg. P

per m³ are found. In the eastern part of the South Atlantic, the phosphate content of the deep water also increases on passing south, but rarely exceeds 60 mg.

TABLE 10. *Phosphate phosphorus in mg. P per m³, in the water at positions along the* 30° W. *meridian of longitude during April–May* 1931

From data, published in *Discovery Reports*, Vol. 4, after correction for salt error.

Depth in metres	57° 36′ S.	53° 33′ S.	46° 43′ S.	38° 10′ S.	21° 13′ S.	3° N.	9° N.	14° 27′ N.
0	62	—	47	5	0	0	0	
20	64	—	47	7	0	0	0	—
40	63	60	47	7	0	0	0	—
60	74	60	48	7	2	0	0	—
80	76	67	52	7	3	15	14	2
100	77	70	55	15	4	42	33	12
150	83	77	60	18	5	46	44	37
200	85	77	65	18	6	50	45	40
400	83	77	67	45	31	69	52	59
800	83	77	81	58	64	77	80	78
1500	80	77	79	86	54	46	53	52
2500	83	77	73	78	42	40	45	45
3200	85	—	—	—	—	—	—	—
3500	—	80	78	82	41	—	46	46
4500	—	—	81	—	55	—	48	48
4900	—	—	—	—	69	—	—	—
5300	—	—	—	—	—	—		50

In the zone of decay concentrations of 65 to 90 mg. P per m³ are encountered, as in the western basin (Clowes, 1938; Deacon, 1933).

The distribution of phosphate in the western basin of the Atlantic has been examined by Redfield (1942). Maximum concentrations in the ocean between 50° N. and 50° S. occur in water characterized by a density lying between limits of $\sigma_t = 27{\cdot}2–27{\cdot}8$; this water is found at depths between 600 and 1000 metres, between these latitudes, and rises steeply to the upper layers on passing into latitudes higher than 50° N. and 50° S. It is considered that this phosphate-rich layer acquired its phosphate partly from organisms falling from above and partly when it was at its sources of origin, the fertile and

relatively phosphate-rich upper layers of higher latitudes. The influence of Antarctic water passing north in the Antarctic Intermediate Current is traced as far as about 15° N., carrying phosphate which existed as such in the Antarctic in addition to phosphate derived from organisms which originated in the Antarctic. The less well-defined phosphate-rich layer in the sub-tropical and temperate North Atlantic is considered due to the decay of organisms within a few hundred metres of the surface in the fertile region about 50° N., this water having drifted south along the surfaces of equal density.

The distribution of phosphate in the Mediterranean is of interest. The water is replenished by surface-layer water from the Atlantic with a low phosphate content, which enters through the Straits of Gibraltar. Mediterranean water of higher salinity which has been concentrated by evaporation passes out through the Straits. This mechanism involves a continuous loss of phosphate. It is found that the concentrations of both phosphate and salts containing nitrogen are low in the deep water of the Mediterranean, compared with the deep water of the open oceans (Thompson, 1931).

Bernard (1939) has followed the changes in phosphate in the upper layers off Monaco, and found that the concentration at the surface rarely exceeds 0·5 mg. P per m^3, while even at a depth of 350 metres it does not rise above 2·5 mg. These upper layers were found to contain a relatively abundant supply of nitrate. At the surface some 50 mg. nitrate-N per m^3 occur and between 400 and 600 mg. at 350 metres (cf. p. 92).

The concentration of nitrogen-containing salts, relatively high compared with that of the phosphate, is attributed by Bernard (1939) to refreshment of the sea with river waters and rain.

In the Adriatic, Ercegovic (1934) has found a seasonal variation in phosphate: the concentration in the surface water changing from less than 0·2 to 3 mg. P per m^3 and at a depth of 90 metres from 1 to 3·2 mg.

Estimation of Phosphate in Solution

The phosphate in solution may be estimated rapidly by the ceruleomolybdate method of Denigès, which was applied to sea water by Atkins (1923).

The customary technique is to add to 100 c.c. of sea water either 1 or 2 c.c. of a solution containing $2\frac{1}{2}\%$ ammonium molybdate and $37\frac{1}{2}\%$, by volume, of concentrated sulphuric acid. (The sulphuric acid is diluted with an equal volume of water and, when cool, mixed with the molybdate dissolved in the remainder of the water; the reagent requires to be kept for one or two days before use and can be stored for many weeks in the dark.) A dilute solution of freshly prepared stannous chloride is then added, the water being kept agitated so as to ensure rapid mixing. The blue colour slowly develops, reaching a maximum at room temperature within about 15 minutes. The colour remains constant for half an hour or more and then slowly fades.

The stannous chloride solution is either made by dissolving 0·05 to 0·1 gm. of the transparent crystals in 25 c.c. of $4N$ hydrochloric acid, when three to four drops are usually required, or by dissolving 0·1 gm. of tin in 2 c.c. concentrated hydrochloric acid with one drop of 3 % copper sulphate and diluting to 10 c.c., when one or two drops are usually required. If too much stannous chloride is added, a yellow or greenish tinge sometimes develops. This makes colour comparison difficult or impossible. If too little stannous chloride is added the blue colour is not fully developed.

In some waters a greenish tinge develops for an unknown reason. It can sometimes be mitigated by filtering the water, by adding a little barium chloride and filtering, and by adding a little sodium sulphite before the stannous chloride.

The intensity of the blue colour which develops bears a linear relation to the phosphate content of the water up to concentrations of 300 mg. phosphate-P per m^3 (Gripenberg, 1929). The intensity developed increases about 1 % for a rise of 1° C. The intensity is reduced by the salts present in sea water.

It is usual to compare the colour developed with that in solutions of phosphate in distilled water, at the same temperature, to which the same quantity of acid-molybdate reagent has

been added. It is then necessary to apply a correction factor owing to the reduced colour formation due to the salts in the sea water.

Various values of this correction for salt error by different observers have been tabulated by Cooper (1938), for waters from the open sea having a salinity of *circa* 35 $^{o}/_{oo}$. Both the quantity of acid-molybdate added to the water and the method of comparison affect the salt error. The following table gives probable values:

Acid-molybdate added c.c. per 100 c.c. sea water	Method of colour comparison	Factor
1	Visual comparison in daylight	1·13
1	Photometer using red light	1·12
2	Visual comparison in daylight	1·35
2	Photometer using red light	1·19

There is evidence that small variations in these values may arise, possibly due to variations in temperature or the concentration of stannous chloride, or some unknown substance in the water itself. The presence of copper in the water reduces the colour formation, but there is insufficient in uncontaminated sea water to have any noticeable effect. Arsenates cause colour formation, but they are absent in natural sea water. Much pertinent information is given by Wattenberg (1937).

Colour comparison is made either visually in daylight or by means of a photometer or photoelectric cell using red light. The Pulfrich photometer is coming into increasing use, but it does not appear to give more exact results than visual comparison when made under the best conditions.

The earlier observations were made between columns of liquid 20 to 25 cm. deep in Heyner cylinders held over a white surface. Some observers still prefer this method of comparison even for waters containing very small concentrations of phosphate. Others can detect a smaller percentage difference in colour intensity when comparing longer columns. Where Heyner cylinders are used it is essential that the bottoms be plane and of quite colourless glass. It is also desirable to compare columns of similar depth; if this is not done allowance may have to be

made for the natural blue colour of the water itself, which approximates to the colour developed in the water by 2 mg. phosphate-P per m^3.

A number of colorimeters have been constructed for use in the laboratory or on board ship, in which columns of liquid up to 60 cm. in length are compared. In some the sea water + reagents is directly compared with standard phosphate solution + reagents, and in others both are compared with some standard coloured solution. The latter arrangement is unsatisfactory, as it may not so readily show up a water which is 'off-tint', a disadvantage which is also shared by photometric methods. It is advantageous that the system be optically balanced, light passing through equal depths of liquid and glass surfaces in the two columns, and it is essential that equal intensities of white light enter the two columns.

If samples of sea water are stored after collection, changes in the phosphate content are likely to take place. It is usual to estimate phosphate within a few hours of collection. Several methods of preservation, as the addition of fluoride or chloroform, have been tried, but are not considered to overcome the difficulty entirely.

Biological Estimation

A biological analysis of the phosphate and available salts containing nitrogen in waters of the North Sea has been made by Schreiber (1927, 1929). Seitz-filtered samples of sea water were inoculated with a green flagellate and exposed to light. The increase in numbers of the plant, which took place with and without additions of known amounts of phosphate or nitrate or both, gave a measure of the available phosphate and nitrogen compounds in the water. The concentrations deduced by this biological analysis were in good agreement with the concentrations found by chemical analysis.

Ammonium-Nitrogen

The distribution of ammonia in ocean waters has not been extensively investigated. Direct Nesslerization after precipitation with alkali (Buch, 1929) or addition of tartrate (Wattenberg,

1937) does not determine quantities below some 10 mg. NH_4-N per m^3. Distillation at atmospheric pressure yields high values, and it is only recently that a method of distillation under reduced pressure devised by Krogh (1934), having an accuracy of 2 mg. NH_4-N per m^3, has been used.

In inshore waters of the Baltic Buch (1920) found from 7 to 40 mg. NH_4-N per m^3, and in waters off the Norwegian coast Braarud & Klem (1931) found varying quantities up to 60 mg. per m^3, there being usually less in the deep water than in the upper layers.

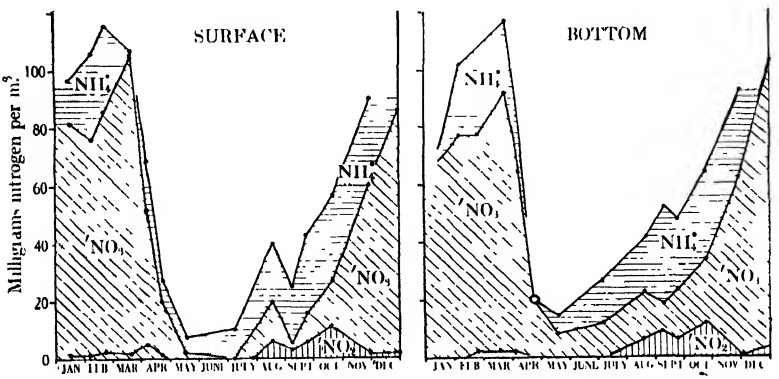

FIG. 18. Variation in ammonium-, nitrate- and nitrite-nitrogen in the upper layers and near the bottom at a position in the English Channel, 20 miles south-west from Plymouth, during 1932.

The seasonal variation of ammonium in the English Channel has been followed by Cooper (1933) and the values, ranging up to some 30 mg. N per m^3, are shown in Fig. 18.

Further inshore higher values were obtained, as much as 200 mg. per m^3 being found close to the land.

In the Arctic, Böhnecke, Foyn & Wattenberg (1932) found from 30 to 50 mg. NH_4-N per m^3 in the surface water, while in an earlier investigation Böhnecke, Hentschel & Wattenberg (1930) found some 25 mg. at the surface with 5 mg. or less in the water below 100 metres.

In the Pacific Robinson & Wirth (1934) found concentrations ranging up to 90 mg. NH_4-N in the upper 50 metres, with smaller quantities in the water below. In inshore waters there was

generally less ammonium. These observations were made during the summer when minima concentrations might be expected in the photosynthetic zone.

The ammonia content of the water at a number of positions in the Gulf of Maine has been investigated by Redfield & Keys (1938) at the beginning and end of summer. They used the precise method of Krogh. In May, quantities ranging up to 45 mg. NH_4-N per m^3 and in September up to 60 mg. were found. In many cases the upper layers were depleted at the surface or a short distance below the surface. In the deeper water stations the greatest concentrations were found in a layer at about 50 metres' depth in May. In this layer nitrite was also present (Fig. 19).

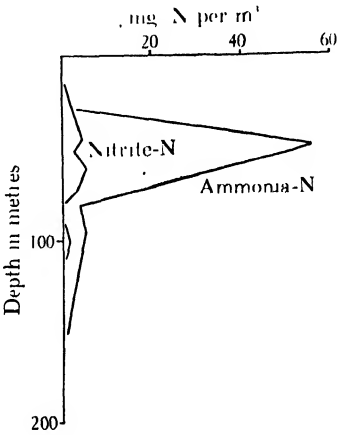

Fig. 19. Concentration of ammonium- and of nitrite-nitrogen in the Gulf of Maine. (After Redfield & Keys, 1938.)

It has been observed by Cooper and others that more ammonium is sometimes found at the surface than in the water immediately below. Buch (1920) pointed out that ammonia is absorbed from the atmosphere in addition to being produced by bacterial action and excreted by animals. Further data concerning ammonium in river waters, rain and snow are given on p. 122.

Nitrite

Nitrite in sea water can be estimated by means of the Greiss-Ilosvay reagent to concentrations as low as 0·02 mg. nitrite-N per m^3.

In inshore waters it undergoes a seasonal variation. In the open oceans it tends to occur in a layer of water below the photosynthetic zone.

At a position in the English Channel, Atkins (1930) found a considerable concentration, some 38 mg. nitrite-N per m^3, in the water below the thermocline but within the lower part of the

photosynthetic layer, during August in 1928. At the same position, Cooper (1933) followed the variation in nitrite throughout the year during 1932 (Fig. 18), finding complete exhaustion in the upper layers in May and July.

Soot-Ryen (1932) has followed the variation throughout the year in two Norwegian fiords, finding complete exhaustion during late winter, and in the upper layers during summer. Maxima, of 4 and 8 mg. nitrite-N per m^3, occurred below the photosynthetic layer in late summer and early autumn.

In the Barents Sea, Verjbinskaya (1932) found that nitrite appeared in the water in spring, concurrently with the onset of plant growth. It reached maxima, of which the highest recorded is 14 mg. N per m^3, below the photosynthetic zone at depths of 50 to 100 metres in August, and completely disappeared from the water towards November.

In the western North Atlantic Rakestraw (1936) has made estimations over a wide area, rarely finding more than 3 mg. nitrite-N per m^3. Maxima usually occurred between 30 and 150 metres from June to September in temperate areas, and in deep water nitrite was frequently absent below this zone.

In the South Atlantic Deacon (1933) reports a layer below the overlying tropical water containing some 30 mg. nitrite-N per m^3. Further south in the Antarctic, where turbulence causes rather complete mixing of the upper layers, the surface water contained nitrite up to 7 mg. N per m^3, while none was found in the deep water.

In the Indian Ocean a thin layer containing nitrite in concentrations up to 20 mg. N per m^3 was usually found at a depth of about 100 metres (Thompson & Gilson, 1937). Below this in the deep water there was either complete absence or less than 1 mg. N per m^3. Low values or complete exhaustion were found in the upper part of the photosynthetic zone. The maxima were most pronounced where the density of the water was increasing rapidly with depth, that is, where the thermocline is most sharply developed.

Nitrate

The great store of combined nitrogen in the sea is in the form of nitrate. It varies in similar manner to the phosphate. Sea water from various localities and depths, from which the nutrient salts have not been reduced to very low concentrations by the phytoplankton, contains between 4 and 13 times more nitrate-nitrogen than phosphate-phosphorus by weight.

Extensive investigations of the nitrate + nitrite content of sea water have been made, using the colour reactions which they give with reduced strychnine and with diphenylbenzidine in the presence of sulphuric acid. The term nitrate in the literature usually includes most of the nitrite present, if any; the nitrite has been investigated in relatively few areas. In the following account 'nitrate' is written in this inclusive sense.

Exhaustion of 'nitrate' due to utilization by the phytoplankton is frequently found in the upper layers in Arctic and temperate regions during the summer. In the South Atlantic in latitudes higher than about 40° S. considerable quantities are found at the surface throughout the year.

The seasonal variation has been followed during the course of several years both in the English Channel (Fig. 18) (Harvey, 1926, 1928; Cooper, 1933), in the Barents Sea (Kreps & Verjbinskaya, 1930, 1932) and off the coast of New South Wales (Dakin & Colefax, 1935, 1940). It follows a similar trend to the seasonal variation in phosphate (Fig. 17).

In the Arctic Böhnecke, Hentschel & Wattenberg (1930) found 270 mg. nitrate-N per m^3 in the water between 300 and 1000 metres in the Irminger Sea, and in the Barents Sea Kreps & Verjbinskaya (1930, 1932) find maxima of 200 to 300 mg. per m^3

Observations in deep water in the temperate North Atlantic are sparse. Rakestraw (1936) records 245 to 330 mg. nitrate-N per m^3 at three positions between 40° and 42° off the American coast. In the Bay of Biscay between 1000 and 3000 metres, 260 to 270 mg. N per m^3 were found (Atkins & Harvey, 1926).

In the South-West Sargasso in 23° N. latitude Rakestraw (1936) records 250 mg. nitrate-N per m^3 at 2000 metres, and 280 mg. between 1500 and 4000 metres at a position further north is given by Rakestraw & Smith (1937).

Nitrate estimations have been made at a series of positions from 15° N. to 55° S., running down the centre of the Atlantic (Deacon, 1933).

TABLE 11. *Nitrate+nitrite-nitrogen in mg. N per m.³ in the water at positions along the* 30° W. *meridian of longitude during April–May* 1931

From data published in *Discovery Reports*, Vol. 4.

Depth in metres	57° 36′ S.	53° 33′ S.	46° 43′ S.	38° 10′ S.	21° 13′ S.	3° N.	9° N.	14° 27′ N.
0	510	—	210	60	2	2	2	3
20	500	—	210	36	0	1	2	1
40	490	490	210	42	0	1	2	1
60	500	490	230	30	0	2	0	1
80	510	490	240	42	0	29	27	1
100	530	500	250	89	1	63	47	28
150	530	510	310	101	1	170	200	170
200	530	530	380	131	7	220	210	200
400	530	540	450	260	100	230	220	210
800	530	540	480	310	240	220	250	240
1500	510	540	450	360	170	220	210	210
2500	510	530	420	330	180	220	210	210
3200	500	—	—	—	—	—	—	—
3500	—	510	450	320	170	—	210	210
4500	—	—	440	—	—	—	210	210
4900	—	—	—	—	280	—	—	—
5300	—	—	—	—	—	—	—	210

After passing 25° S. the 'nitrate' content of the deep water below about 500 metres increased with increasing latitude, rising from some 200 mg. N per m.³ to 500 mg. in 50° S. This increase in nitrate with latitude is more rapid than the increase in phosphate. Similar high concentrations of nitrate have also been found in the Antarctic by Ruud (1930), who records 400 to 600 mg. N per m.³

ESTIMATION OF NITRATE

Two rapid methods of estimating, approximately, the nitrate +nitrite in sea water have been developed. Both strychnidine and diphenylbenzidene form intensely coloured compounds with nitrate in the presence of concentrated sulphuric acid. Under

controlled conditions the intensity of colour is directly proportional to the nitrate; any nitrite present acts in a similar manner but does not cause as much colour formation as equivalent quantities of nitrate. Both reagents are converted to the coloured compounds by other oxidizing agents in the presence of sulphuric acid, but none such occur in sufficient quantity in sea water.

The presence of organic matter in solution, or of appreciable amounts of plankton organisms, reduces the colour formation. Neither method is therefore suitable for polluted or some inshore waters. At times, when phytoplankton is abundant, it is necessary to filter or centrifuge the sample before proceeding with the estimation.

Strychnidine (isolated from the electrolytic reduction products of strychnine by Tafel & Nauman in 1901) gives an intense red colour with solutions of nitrates in the presence of sodium chloride after adding an equal volume of concentrated sulphuric acid. The red compound is rapidly bleached in strong light. Strychnidine is not on the market; mixed products, prepared by reducing strychnine sulphate with amalgamated zinc and hydrochloric acid, are diluted with sulphuric acid and used as reagent.

The reagent may be prepared as follows. After washing with dilute acid, 100 g. of pure granulated or sheet zinc are amalgamated by adding dilute mercuric chloride and again washed. To this are added 2 g. of strychnine sulphate, a little water which has been distilled from alkali and 50 c.c. of hydrochloric acid. It is kept for 12 to 36 hours on a water bath, three further 50 c.c. lots of hydrochloric acid being added at intervals. The water bath requires to be electrically heated and away from any flame or other source of contamination with oxides of nitrogen. The final product is cooled, the remaining zinc removed, and without delay 600 c.c. of concentrated sulphuric acid are added. This is best done in the open air, since much hydrochloric acid is evolved. After standing, the white zinc chloride settles leaving a clear solution, which is decanted into brown glass bottles and kept, preferably in the dark. After keeping for 2 or 3 days, the reagent is ready for use.

On adding 6 c.c. of this reagent to 5 c.c. of distilled water, no

more than the faintest pink tint should develop when the mixture is kept for 18 to 24 hours in the dark. If more colour develops, this shows contamination of the reagent with oxides of nitrogen. Such have frequently been found in the sulphuric acid, once, at least, in the strychnine sulphate, and may take place through absorption from the atmosphere or solution from white glass vessels. It is then necessary to start again with a different supply of sulphuric acid.

On adding 6 c.c. of the reagent to 5 c.c. of distilled water containing 100 mg. nitrate-N per m^3 a rose colour should develop and attain after 18 to 24 hours in the dark an intensity as great as in a 0·0008 % solution of safranin (Grübler). Different batches of reagent differ considerably in 'strength', which tends to increase on keeping.

Manufacture of a 'strong' uncontaminated reagent is largely a matter of luck. A product put on the market by a leading continental firm of chemical manufacturers proved very variable. The reagent has now been prepared and used by many investigators, usually after initial trouble in finding a source of sulphuric acid free from oxides of nitrogen.

Having made a batch of reagent, it is then necessary to determine the limits within which the concentration of nitrate is proportional to the intensity of colour developed. Varying amounts of nitrate are added to a sea water; 5 c.c. lots are treated with 6 c.c. of the reagent, and left in the dark for 18 to 24 hours, together with 5 c.c. of water (distilled from alkali) + reagent to provide a 'reagent blank'. The colours are then compared in an ordinary colorimeter by artificial light. By assigning the value of 100 arbitrary units of colour to one of the series, the units of colour produced in the others are calculated. Fig. 20 shows the results of such a determination, where the reagent was sufficiently 'strong' to give linear relations with concentrations up to 120 mg. nitrate-N per m^3.

In carrying out estimations it is sometimes necessary to dilute the sample of sea water so that its 'nitrate' content lies within the prescribed limits for the particular batch of reagent in use. As little as 1 mg. nitrate-N per m^3 can be readily detected with a 'strong' batch of reagent having a low 'reagent blank'.

A variety of methods for the colour comparison and calculation

of the 'nitrate' content have been in use. Probably the most exact method is to add one or more known quantities of nitrate to 5 c.c. portions of the sample, make colour comparisons *inter se* and with a reagent blank, and to plot the results, as in Fig. 21,

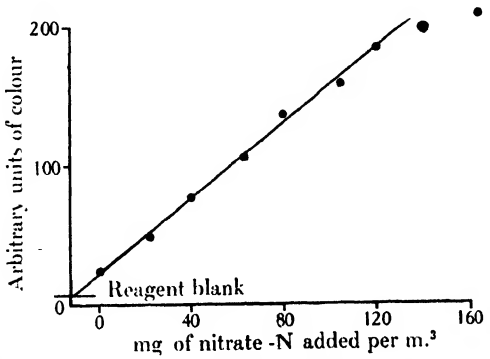

FIG. 20. Diagram showing relation between red colour developed and 'nitrate' content of sea water.

where *OA* indicates the concentration in the water sample as being 15 mg. per m.³ This procedure reduces any error which may be due to dissolved organic matter affecting colour formation in some of the water.

The original papers concerning this method of estimation contain many details of procedure (Harvey, 1926, 1929; Cooper, 1932; Wattenberg, 1937).

Diphenylbenzidene, which is on the market, is used in the method of estimation developed by Atkins (1932), after being recrystallized from boiling toluene. The method has been used by Riley for North Atlantic waters. 2·5 c.c. of sea water are mixed with 6 c.c. of concentrated sulphuric acid. After cooling, 1·5 c.c. of a 0·02 % solution of diphenylbenzidene in concentrated sulphuric acid are added, care being taken that the rate of addition and mixing are the same in all cases. A blue colour develops and

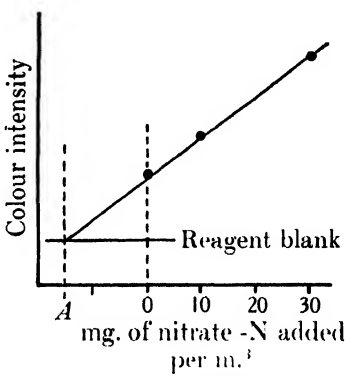

FIG. 21. Diagram illustrating method of estimating nitrate in sea water.

colour comparisons are made after 20 to 24 hours. The blue colour is stable to light; the salts in sea water increase the colour formation by about 20% over that in fresh water; nitrites are converted to nitrous acid on adding the sulphuric acid, and there is liable to be some loss of nitrous acid if the mixture is not rapidly cooled.

It is usual to sterilize the water samples with mercuric chloride when they are collected, if estimations are to be made at a later date.

The N/P Ratio

A roughly proportional relation between the nitrate and phosphate in sea water became apparent soon after investigations of the distribution and seasonal variation of these two constituents were started. It was considered that plant organisms utilized these in the same proportion as they occur in the sea, since they are almost completely used up by the phytoplankton in the upper layers during summer (Harvey, 1927). Redfield (1934) examined analyses of waters from the Atlantic, Indian and Pacific Oceans; these showed a ratio of nitrate-nitrogen to phosphate-phosphorus which varied around 6·7, after applying a correction for salt error to the phosphate determination. Analyses of phytoplankton from the Atlantic yielded eight times more nitrogen than phosphorus; later analyses of diatoms by Cooper (1937) also yielded between 6·8 and 9·2 times more nitrogen than phosphorus. The latter author has tabulated much existing data of the N/P ratio in ocean waters, and found that certain bodies of water are distinguished by either high or low ratios. He also notes a marked change in the ratio which had taken place in the English Channel between 1925 and 1932—over a period during which a marked change had also taken place in its general fertility (p. 152).

A line of stations extending from the Antarctic along the 30° W. meridian to 14° N. provides values of the N/P ratio which are shown in Table 12. The Antarctic Deep Water (Fig. 4) shows a materially higher ratio than the Atlantic Deep Water, which is of Polar origin; this high ratio is also shown at intermediate depths at 38° S. latitude, having been carried north in the Antarctic Intermediate Current. Very low ratios are found in

the water below the photosynthetic zone in the low latitudes; similar low ratios are often found in the North Atlantic at similar (shallow) depths. It may be due to direct regeneration of phosphate being more rapid than indirect regeneration of nitrate at these levels (pp. 117, 121).

TABLE 12. *The ratio of nitrate-nitrogen to phosphate-phosphorus by weight, April–May* 1931

Data from *Discovery Reports*, Vol. 4, 1932. Phosphate values corrected for salt error. Longitude 30° W.

Depth in metres	57° 36′ S.	53° 33′ S.	46° 43′ S.	38° 10′ S.	21° 13′ S.	3° N.	9° N.	14° 27′ N.
0	8·2	—	4·5	—	—	—	—	—
20	7·8	—	4·5	5·2	—	—	—	—
40	7·8	8·2	4·5	6	—	—	—	—
60	6·8	8·2	4·8	4·3	—	—	—	—
80	6·7	7·3	4·6	6	—	1·9	1·9	—
100	6·9	7·1	4·6	5·9	—	1·5	1·4	2·3
150	6·4	6·5	5·2	5·6	—	3·7	4·5	4·6
200	6·2	6·9	5·9	7·3	1·1	4·4	4·7	5·0
400	6·4	7·0	6·7	5·8	3·2	3·3	4·2	3·7
800	6·4	7·0	5·9	5·3	3·7	2·9	3·1	3·1
1500	6·4	7·0	5·7	4·2	3·1	4·8	4·0	4·0
2500	6·1	6·9	5·7	4·2	4·3	5·5	4·7	4·7
3200	5·9	—	—	—	—	—	—	4·5
3500	—	6·4	5·8	3·9	4·1	—	4·7	4·4
4500	—	—	5·4	—	—	—	—	—
4900	—	—	—	—	4·1	—	4·4	—
5300	—	—	—	—	—	—	—	4·2

It is noteworthy that the Atlantic Deep Water has a ratio ranging around 4·5. Further north data are scanty, but at a position off Bermuda, the deep water which lies below the Gulf Stream water has a ratio ranging around 5·8, and in the Irminger Sea in 63° N. of 6·6. Further north in the relatively shallow Barents Sea in 70° to 76° N. the ratio varies between 6·5 and 14.

It therefore appears that the N/P ratio in the Atlantic Deep Water decreases as the water drifts south from polar regions until, after several years, it finally mixes with and merges into the high ratio Antarctic Deep Water. The diminution in the ratio appears to be due to decrease in the 'nitrate' content of the water, rather than to a change in its phosphate content. If

this is indeed so, it suggests that denitrification may take place during the slow southerly drift.

In the eastern North Atlantic the picture is complicated by Mediterranean water which spreads out into the Atlantic, mostly as an intermediate layer between some 600 and 1200 metres. The Mediterranean water has a singularly high ratio, 10 at the western rising to 16 at the eastern end. Off the Iberian Peninsula and even in the Bay of Biscay admixture with this high ratio water is apparent.

The setting free of phosphate and of ammonium in the sea by decomposition of organic matter, and the interconversion of salts containing nitrogen, is bound up with the activities of bacteria. It is therefore necessary to summarize present knowledge concerning these organisms before discussing the cycle of events which orders the distribution of these salts in the oceans.

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VIII. CHANGES DUE TO BACTERIA

The Bacterial Flora

The sea contains bacteria freely suspended in the water, attached to organisms, to particles of organic debris, and in the superficial layer of the sea floor where they are abundant. In mud or sand the numbers decrease with depth below the superficial layer, many spore-forming species being present (Waksman, Reuszer, Carey, Hotchkiss & Renn, 1933).

Bennecke (1933) and ZoBell & Upham (1944) give a very complete bibliography of the species of marine bacteria which have been isolated and described, some from sea water and others only from bottom deposits. Many of these species have been found to bring about chemical changes in the culture media, but it is improbable that all of them act in the same manner in the sea. To do so, some of the species are known to require the conditions of culture, such as plentiful food or ample supply of some constituent which is only at great dilution in the sea.

Table 13. *Some changes brought about through the agency of marine bacteria in the sea or in culture*

Decomposition of	chitin
	cellulose
	petroleum hydrocarbons
	lignin
	urea
Oxidation of	ammonium to nitrite
	nitrite to nitrate
	sulphide to sulphate
Reduction of	nitrate to nitrite
	nitrate to nitrogen gas
	sulphate to sulphide (anaerobic)
	sulphides to sulphur
Utilization of	gaseous nitrogen
	ammonium and urea
	nitrate and nitrite
	phosphate
as source of nitrogen and phosphorus in the bacterial cell, and liberation of these as ammonium and phosphate after death	
Formation of concretions consisting of iron and manganese oxides	

The population density of bacteria decreases on passing from inshore waters to the open sea. In the open ocean the greatest population is found where phytoplankton is abundant, and in the water immediately above the sea floor, particularly over a sand or shell bottom. Observations by Waksman, Reuszer, Carey, Hotchkiss & Renn (1933) point to the development of phytoplankton in the sea being closely accompanied by the development of planktonic bacteria. The plants are grazed by animals which do not fully digest the cell substance when food is plentiful, and thus nutrient material is excreted into the water.

In the Mediterranean, Bertel (1912) records that bacteria increase in numbers with depth, while at the surface they are mostly killed by strong sunlight to be replaced by others during the night.

In clear inshore waters several hundred or more bacteria per c.c., comprising 25 to 35 species, are usually found. In the open ocean away from land the number may drop to less than 10 per c.c. where phytoplankton is sparse.

The bacteria which persist in suspension in sea water utilize nutriment at great dilution, there being no more than 2 to 5 mg. of available organic matter per litre. They are also adapted to growth in the relatively high concentration of salt. The following table indicates that only some 10% of bacteria from the open ocean will live in fresh water, while many terrigenous bacteria which have become adapted to salt water are to be found close inshore.

TABLE 14. *Relative numbers of bacteria from marine and terrestrial sources which developed in a nutrient medium prepared with sea water and fresh water*

Source of inocula	Sea water +nutrients	Fresh water +nutrients
Raw sea water	100	9
Inshore water, terrigenous pollution	100	97
Tap water	4	100
Inland soil	15	100
Soil near sea	48	100
Sewage	13	100

From ZoBell (1941).

The majority of freshwater bacteria soon perish in the sea. Great numbers of coliform bacteria are discharged in sewage but are not found in the sea more than a few miles from the outfalls. Pathogenic bacteria have only a short life in sea water; however, if typhoid bacilli are filtered out from the water by shellfish, they may remain alive for some weeks in the fluids within the shell.

A variety of methods have been employed to estimate the total number of bacteria in sea water. An extensive study of the number of cells and of species which grow in a variety of nutritive media has been made at the Scripps Institution, with the object of obtaining maximum plate or dilution counts (ZoBell, 1941). It was found that most of the bacteria in sea water and in bottom deposits, at positions remote from the influence of land drainage, have specific salt requirements which are best satisfied by natural sea water. Neither synthetic sea water containing all the major constituents (p. 29) nor other isotonic salt solutions are satisfactory substitutes. The further addition of iron to natural sea water led to increased bacterial development, in some cases to an increase amounting to 76%, and to the development of a greater number of species. There were indications that the addition of phosphate led to slightly greater development. Successive dilution-method counts using sea water to which had been added 0·5% of bacto-peptone and 0·01% of ferric phosphate gave values 12% higher than plate counts in the same medium with 1·5% bacto-agar. A considerable variety of nutrients was tried and found to give either inferior or no higher counts than the above. The optimum *p*H range lay between 7·5 and 7·9.

During the course of this investigation it was observed that bacteria behave differently in sea water collected from different positions, enriched with nutrients and sterilized at 120° C. These differences in growth-promoting properties disappeared if the water was first stored at room temperature for a few weeks, presumably because the organic fractions which are responsible for the differences are oxidized by the increased bacterial activity accompanying the storage of water in glass bottles.

With regard to other methods of estimating the bacterial population in samples of sea water, direct observation is difficult,

since it is necessary to concentrate the cells. It yields higher counts than are obtained by plate or dilution methods (Cholodny, 1929), and presumably includes some cells which do not grow in the nutritive media employed in the culture methods and some dead cells which have not completed autolysis.

When a glass slide is hung in the sea, bacteria rapidly attach themselves to the surface; the number of cells which attach under standardized conditions bears a direct relation to plate counts (Hotchkiss & Waksman, 1936).

The temperature for most rapid multiplication lies in the neighbourhood of 20° C. for most marine bacteria (ZoBell & Upham, 1944). These authors also state that ability to grow at subzero temperatures is a common property of most marine bacteria and that their thermal death point is considerably below that of most terrigenous or freshwater bacteria. Ten minutes at 30° C. killed about one-quarter of the bacteria collected from cold deep ocean water, and ten minutes at 40° C. killed more than three-quarters.

Effect of Storage on Bacterial Flora

The study of changes taking place in sea water under natural conditions in the oceans is hampered by the remarkable events which happen when sea water is stored in a glass vessel. Whipple reported in 1901 that when tap water was filled into glass bottles the number of bacteria fell during the first 3 to 6 hours by 10 to 25%, and later increased by many hundred per cent, with a reduction in number of species. This rise in bacterial numbers was several times greater in small than in large bottles, and was reduced or even nullified if the water was kept agitated. A similar rise in bacterial numbers takes place when sea water is stored in glass vessels. Waksman & Carey (1935) found that multiplication took place in Seitz and in colloid-filtered water which had been inoculated with raw water, and from the oxygen used calculated that the rapid growth of bacteria breaks down about one-third of the organic matter in solution. ZoBell & Anderson (1936*a*) and Lloyd (1937) found a much greater increase in numbers of bacteria when the water was stored in small than in larger bottles, or in bottles where the water-glass surface had

been increased by filling the bottle with glass beads or rods. By observing the numbers at close intervals of time, Miss Lloyd found that the increase followed the course of a population curve; the peaks were determined by the volume of the container, but were not affected by the surface area of the water exposed to the air. ZoBell & Anderson found that the peaks, or maximum number of bacteria found in the water, showed a rough direct proportion to the volume/surface area of the bottles, the maxima in small vessels being about twice the maxima in vessels ten times as large. They also observed that, when the surface area was increased by a shallow layer of glass beads or silica grains, the resulting increase in numbers of bacteria was less than that calculated from the volume/area ratio. They concluded that not only this ratio, but also the proximity of the main body of water to the glass surface, played a part. The greatest increases were found in water between sand grains where populations of some twelve million bacteria per c.c. developed in water which maintained no more than a few hundred bacteria per c.c. in the sea.

Whipple had found that the marked difference between maximum bacterial population, which arose when tap water was stored in small and in large bottles, was much reduced if a small quantity of peptone (5 mg. per litre) was added to the water. ZoBell & Anderson noted that if nitrite and 10 mg. per litre of peptone were added to sea water, there was a greater and more rapid loss of nitrite in smaller than in larger vessels, but no such difference when 100 mg. per litre of peptone was added. It appears that the volume effect only occurs when bacteria develop in water containing food substances at very great dilution. This conclusion was also reached by Heukelekian & Heller (1940), who found no growth of the bacterium *Escherichia coli* in solutions containing 0·5 and 2·5 mg. per litre of glucose and peptone, but growth did occur if glass beads were added. With 25 mg. per litre growth took place without the addition of glass beads, and with concentrations greater than this the effect of adding glass beads faded out.

As Whipple had found for tap water, so ZoBell & Anderson found a reduction in number of species when sea water was stored. Some twenty-five to thirty-five species were generally

found immediately after the water had been collected, falling to nine or ten species by the time bacterial numbers had reached a maximum and to no more than four or five species after the maximum population had declined. After this decline the population remained relatively high for a long period, the numbers fluctuating from a few thousand to over a hundred thousand per c.c.—a sample of sea water which had been stored at 2° to 6° C. for 4 years was found to contain 209,000 bacteria per c.c.

Both ZoBell & Anderson (1936) and Waksman & Renn (1936) observed that in full and stoppered bottles the consumption of oxygen continued undiminished for some time after the bacteria in the water had reached maximum numbers and while the population was falling. The former investigators have shown that great numbers of bacteria develop on the glass surfaces; one experiment indicated that within 24 hours more than twice as many were attached to the surface of the glass as were in the water. This accounts for the continued consumption of oxygen after the number of bacteria in suspension have declined.

TABLE 15. *The oxygen content of sea water stored at* 16° C. *in glass-stoppered bottles of different capacities after* 20 *days, and the maximal bacterial population reached* (*after* 3 *to* 5 *days*) *in similar bottles*

The water initially contained 5·46 c.c. O_2 per litre and 231 bacteria per c.c.

Volume of sea water (c.c.)	10	100	1000	10,000
O_2 per litre	2·59	2·90	3·68	4·17
Bacteria per c.c.	1,475,000	1,080,000	673,000	382,000

ZoBell (1936), *Proc. Soc. Exp. Biol., N.Y.*, **35**, p. 271.

In ZoBell & Anderson's investigation a series of experiments was made dealing with the effect of oxygen on the proliferation of bacteria in stored sea waters. No material effect was observed unless the water was less than 50 % saturated with air. Waksman & Carey, on the other hand, observed greater growth in fully aerated than in partially aerated water. This was confirmed later by Waksman & Renn (1936). Subsequent observations by

ZoBell (1940) led to the conclusion that the rate of oxygen consumption was independent of the partial pressure of oxygen between 0·31 and 12·74 c.c. per litre at 22° C.

Most of the experimental observations have been made with sea water from which only the larger plankton organisms have been removed, leaving nannoplankton. However, both Keys, Christensen & Krogh (1935) and Waksman & Carey (1935) have filtered sea water through collodion ultrafilters, removing all plankton and colloids, and found that about as many bacteria developed in this, after reinoculation, as in the unfiltered water. Removal of the plankton and bacteria by Seitz or membrane filtration reduces the oxygen consumed after reinoculation, but not always to a very marked degree. It leads to a higher rate of bacterial multiplication, due perhaps to the removal of phagocytic protozoa.

The proliferation of bacteria when water is enclosed in glass vessels and the effect of their size is attributed by ZoBell & Anderson to the water-glass surfaces:

(i) Providing a resting place for periphytic bacteria, many marine species having periphytic tendencies and at least some being obligate periphytes. In this connection it is pertinent that saprophytic bacteria are attached to suspended particles in the sea (Lloyd, 1930) and that bacteria are most numerous where plankton is most abundant, as observed by Waksman, Reuszer, Carey, Hotchkiss & Renn (1933), who consider that 'bacteria exist only to a very limited extent in the free water of the sea, but are largely attached to the plankton organisms'.

(ii) Concentrating organic substances from very dilute solution on the surfaces owing to adsorption or other physical attraction.

(iii) Retarding the diffusion of bacterial enzymes away from the cell, where the cell is attached to a solid surface; it has been generally observed that attachment to particles exerts a favourable influence on their enzymatic activity.

Regarding the second suggestion—that organic matter in solution is adsorbed on solid surfaces—the authors state that the accumulation of a film of organic matter on glass slides soon after being submerged in sea water can be demonstrated by differential stains as well as by microchemical technique. Stark, Sadler & McCoy (1938) also state that an accumulation of

organic matter can be detected on glass slides which have been immersed for several hours in lake water. Their method of detection was based on the oxidation of a sulphuric acid-dichromate mixture. In neither of these communications is the exact technique described. The writer has been unable to obtain definite results on these lines, but a number of observations have been made which point, indirectly, to adsorption taking place (Harvey, 1941).

With regard to the third suggestion, that bacterial enzymes diffuse from the cell into the surrounding water, the following observations are of interest. Kreps (1934) found that changes in ammonium and in nitrate took place in water which had passed a Seitz filter or been sterilized with mercuric chloride. He suggests that sea water, particularly water near the bottom where organic matter is decomposing, contains enzymes which bring about these changes. Keys, Christensen & Krogh (1935) have also observed changes in the ammonium content of water which had been sterilized with mercuric chloride, while Newcombe & Brust (1940) have noted that saturating water with chloroform reduces but does not stop phosphate being set free during storage. Cooper (1937) has also found changes in the ammonium content of water sterilized with mercuric chloride.

It is an outstanding question why offshore sea water, which contains sufficient nutriment for the production of several million bacteria per c.c., and will in fact rapidly produce this population when in contact with clean sand grains, normally supports a population of no more than 10 to 200 bacteria per c.c. as free-living planktonic cells. In addition to lack of solid surfaces, protozoa and other animals keep the bacterial fauna eaten down; this has been stressed by both ZoBell and by Waksman & Hotchkiss (1937). The former investigator (1936) has also concluded that natural sea water contains a bacteriophage, or heat-labile substances inimical to the growth of bacteria; added bacteria grew more rapidly in autoclaved than in Berkefeld filtered sea water. There is some natural brake upon the growth of planktonic bacteria in the open sea.

Chemical Changes taking place during Storage

Before discussing the changes which take place in sea water during storage it is helpful to consider in broad outline the food requirements and fate of planktonic bacterial cells.

Given suitable conditions and a sufficiency of food, the bacteria continue to build up cell substance and to divide. Their cell substance is singularly rich in both nitrogen and phosphorus. Waksman & Carey (1935) give the ratio of carbon to nitrogen as 5 to 1, while Waksman, Hotchkiss, Carey & Hardman (1938) find that four and a half times more nitrogen than phosphorus is utilized by marine bacteria during growth. These observations indicate a ratio of 45 carbon : 9 nitrogen : 2 phosphorus in the bacterial cell.

Meanwhile the growing bacterial cell respires, consuming oxygen and liberating carbon dioxide. The rate of respiration varies with different species of marine bacteria (Johnson, 1936), with the concentration of available food (ZoBell, 1940) and with temperature. The rate is singularly rapid; thus ZoBell calculates that 1 g. of actively growing marine bacteria consumes some 30 c.c. of oxygen per hour at 22° C., whereas marine animals are stated to consume 0·002 to 1·0 c.c. of oxygen per hour per gram of living tissue.

Provided the environment remains suitable and there is sufficient food, the bacteria continue to respire, build up cell substance and divide.

If the organic matter in solution used as food contains nitrogen or phosphorus in excess of the bacteria's requirements, a part, if not all, of this excess is split off as ammonium or phosphate.

If the organic matter used as food is insufficiently rich in nitrogen or phosphorus, some species obtain their nitrogen requirement from ammonium in solution, some from nitrate or nitrite, while some species can obtain their phosphorus from phosphate in solution.

When the food supply runs out or conditions become unsuitable the cells die and autolyse, giving off into the surrounding water part of their contained nitrogen as ammonia, all or nearly all their phosphorus as phosphate, and much of their contained carbon as carbon dioxide. A small residue may remain which

eventually falls to the bottom as 'marine humus'. Once death has taken place autolysis proceeds rapidly. The experiment shown in Fig. 23 indicates that all, or almost all, the phosphorus in the bacterial cells was returned to the water within a week after the food supply for the bacteria had run short. Besides death and autolysis, many bacterial cells doubtless end their existence by being eaten and digested by protozoa and filter-feeding animals.

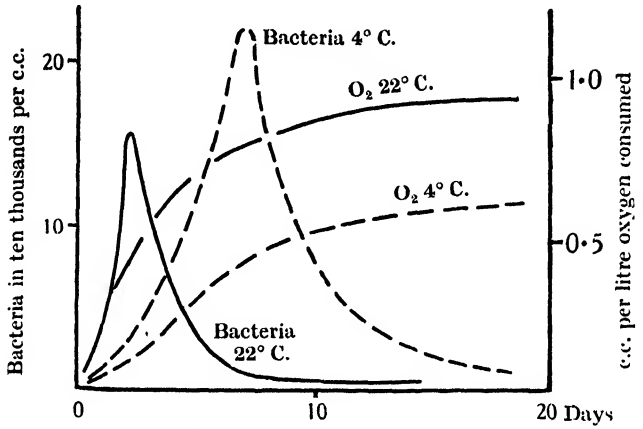

FIG. 22. Diagram showing the change in bacterial population and the consumption of oxygen in stored sea water at 4° C. and at 22° C. (After Waksman & Renn, 1936.)

A conception, such as that outlined in the preceding paragraphs, throws light upon the changes which take place during the storage of sea water, or of sea water to which dead plankton or organic compounds have been added.

The change in oxygen content of raw sea water, containing small plant and animal organisms as well as bacteria, has been followed by several observers for storage periods up to about 3 weeks. A rapid consumption of oxygen and proliferation of planktonic bacteria is followed by a slower consumption, due mostly to bacteria adherent to the glass (Fig. 22). The oxygen consumption during the first 5 days, when fresh or sea water is stored, is usually about half the consumption at the end of 3 weeks. The continued consumption after this has been little investigated; two experiments by Waksman & Renn (1936) lasting 9 weeks show that it continues slowly.

The quantity of oxygen consumed by raw water, collected from different positions, when stored in the dark at the same temperature, varies considerably. The samples of water will contain varying quantities of minute plants and animals; there is evidence that the dissolved organic matter also varies. Relatively low values of oxygen consumption in offshore waters are recorded—values of *circa* 0·5 c.c. oxygen per litre, compared with over 1 c.c. consumed by inshore water which had been filtered free from all organisms and reinoculated in experiments by Waksman & Carey (1935).

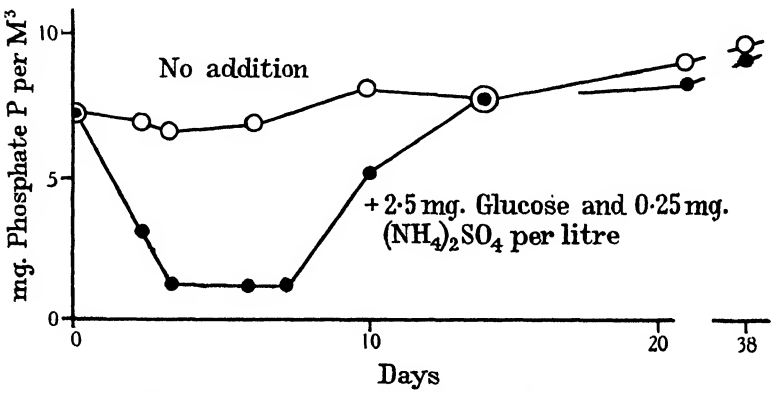

FIG. 23. Changes in phosphate concentration during storage in a sample of sea water, filtered through Whatman No. 3 paper. The lower curve shows the effect of increased bacterial growth due to the addition of phosphorus-free nutrient.

In general, samples of inshore water consume more oxygen than samples from the open sea, where water from great depths consumes more oxygen than water from the upper layers (Seiwell, 1937). Temperature plays a predominating part in controlling the rate of consumption. Johnson (1936) records Q_{10} for washed marine bacteria varying between 2·2 and 2·3, values which agree with observations by Seiwell (1937), who gives the following data:

Average oxygen consumption of all samples stored in the dark,

at 24° C., 1·224 c.c. O_2 per litre,

at 11° C., 0·487 ,, ,, ,,

The rate of consumption in raw water from the upper layers of the sea is sometimes reduced through insufficient phosphorus

for the bacterial requirements, and may be increased by the addition of phosphate (Keys, Christensen & Krogh, 1935). There is sufficient available nitrogen for the bacteria; addition of ammonium has no effect.

The change in *p*H due to carbon dioxide set free in raw waters has been followed by Atkins (1922). The least change corresponded to the production of 0·9 mg. C per litre—about one-half of the total organic carbon thought to be present as organic compounds in solution in ocean water.

An increase in phosphate during storage of raw water has been recorded by several observers, sometimes preceded by a decrease due to utilization by bacteria where the organic food contains insufficient phosphorus.

The ammonia in solution usually decreases when sea water is stored in the dark; in some waters an increase has been observed (Keys, Christensen & Krogh, 1935; Cooper, 1937*a*). Such changes also take place in waters sterilized with mercuric chloride or by filtration. Cooper has observed a reduction in ammonia after 13 days' storage in a series of samples from the open sea, with no corresponding increase in nitrite. He considers that ammonium is oxidized to hyponitrite, the reaction being activated by some agency which is not necessarily bacterial since sterilization does not stop it.

Increases in the nitrite and nitrate content have not been found in water collected from offshore, although looked for by several observers, unless contaminated with bottom deposit (see Carey, 1938). This is odd, because the distribution of nitrite and ammonia in the oceans indicates that both nitrite and nitrate are formed in the layer of water poor in oxygen below the photosynthetic zone. Two possibilities suggest themselves: either the nitrite- and nitrate-forming bacteria die out during storage of more or less plankton-free water (Harvey, 1941), or these bacteria are only active when attached to plankton. If dead plankton is added to raw water, both nitrite and later nitrate are slowly formed (Carey, 1938; Von Brand & Rakestraw, 1937–1942).

Bacterial Decomposition of Organic Compounds and of Dead Plankton Organisms added to Sea Water

When a bacterial food devoid of nitrogen, such as a sugar, is added to sea water, the rate and quantity of oxygen consumed, due to the growth of bacteria, is increased. The available nitrogen in the water, added to that liberated by decomposing nitrogenous organic matter in solution, allows part of the added sugar to be utilized rapidly.

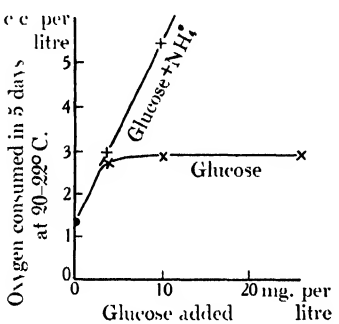

Fig. 24. The effect of adding glucose and of adding glucose + ammonium on the oxygen consumed by bacteria in a sample of inshore sea water.

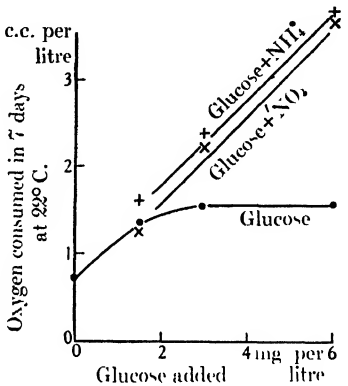

Fig. 25. The effect of adding glucose, glucose + ammonium and glucose + nitrate on the oxygen consumed by bacteria in a sample of inshore sea water.

Waksman & Carey (1935), in experiments with an inshore water which consumed 1·3 c.c. of oxygen per litre in 5 days, found that the oxygen consumption was doubled on adding 2·5 mg. per litre of glucose, but that further additions of glucose caused no further additional consumption unless a source of nitrogen was also added (Fig. 24). They made two inferences from this and other experiments: (i) since the oxygen consumption due to 2·5 mg. of added glucose was equal to the oxygen consumption of the raw water, the latter contained a similar quantity (2·5 mg. per litre) of readily available organic matter; (ii) since the increased oxygen consumption was two-thirds of the quantity required for the complete oxidation of the 2·5 mg. per litre of sugar, about two-thirds had been used in

respiration and one-third built up into bacterial tissue which remained unautolysed at the end of the 5 day period.

A similar experiment with an inshore water (Fig. 25) showed that the addition of 1·5 mg. per litre of glucose doubled the oxygen consumption.* Larger additions of glucose led to no greater oxygen consumption in the 7 day period, unless an additional source of nitrogen was provided. Ammonium appeared to be rather more readily utilized than nitrate. The increased oxygen consumption due to the addition of 1·5 mg. glucose was again two-thirds of the quantity required for complete oxidation of the sugar (Waksman & Renn, 1936).

The increased development of bacteria and consumption of oxygen due to the addition of various amino-acids has been investigated by Waksman & Renn (1936). In 5 days at 20° C. between 50 and 70% of the oxygen required for complete oxidation was consumed. A more detailed study of the breakdown of asparagine has been made by Waksman, Hotchkiss, Carey & Hardman (1938). In from 6 to 9 days at room temperature some 70% of the oxygen required for complete oxidation was consumed and a similar proportion of the contained nitrogen was liberated as ammonium.

A few experiments have been made concerning bacterial decomposition of other substances added to sea water and the liberation from them of ammonia or phosphoric acid. The addition of urea, uric acid or trimethylamine did not lead to a rapid liberation of ammonia. Nucleic acid was rapidly broken down, setting free phosphoric acid, while casein was less rapidly decomposed. A single experiment with glycerophosphoric acid yielded no phosphate (Harvey, 1940).

The rapid decomposition of dead zooplankton added to sea water has been recorded by several observers. Waksman, Carey & Reuszer (1933) found that at 16° to 20° C. in 19 days about one-half the nitrogen in the dead animals was liberated as ammonium and about one-fifth of the carbon as carbon dioxide. A similar experiment by Waksman, Hotchkiss, Carey & Hard-

* Analyses by means of direct combustion indicate that sea water contains *circa* 5 mg. organic matter per litre. The above values of oxygen consumption suggest therefore that one-fourth to one-half of the organic matter in solution is readily decomposed. The water of Lake Mendota contains *circa* 12 mg. per litre of organic matter, and about one-third of this is readily decomposed by bacteria (ZoBell, 1940). The similarity in proportionate values is noteworthy.

man (1938) showed rapid liberation of ammonium and phosphate. Seiwell & Seiwell (1938) record rapid initial liberation of phosphate which soon became slower, with marked diminution in size of the particles of detritus. Cooper (1935) has followed the liberation of phosphate from zooplankton in water at 14° to 19° C. for a period of several months. A rapid initial liberation was followed by a lull; later a second liberation occurred, leading to a maximum phosphate content of the water at the end of 2 months. The quantity of phosphorus liberated as phosphate was considerably in excess of the quantity in the added zooplankton. This suggests that the plentiful bacterial food allowed the growth of species of bacteria which decomposed phosphorus containing organic substances in solution in the water. When the waters were stored without added zooplankton there was no increase in phosphate comparable in quantity to this excess.

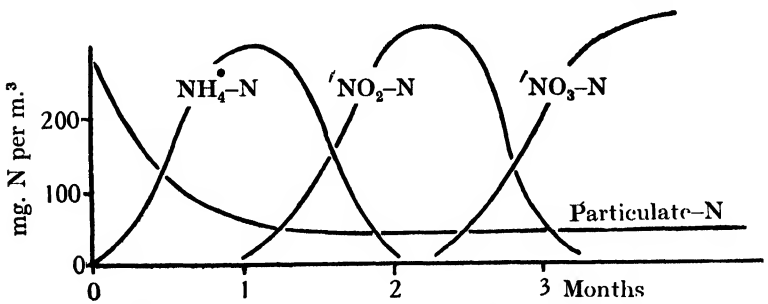

FIG. 26. Diagram showing the production of ammonium, followed by its conversion to nitrite and finally to nitrate, in sea water containing diatoms while stored in the dark. (After Von Brand & Rakestraw.)

Several studies have been made concerning the decomposition of phytoplankton. Von Brand & Rakestraw (1937–1942) added living diatoms, grown in culture, to sea water, and stored this in the dark for several months, keeping it aerated. Initial analyses gave the quantity of nitrogen in the added diatoms and any particles of organic matter present in the water. After about one month—the period varying with the temperature for the most part—a quantity of ammonium-nitrogen had been set free into the water, equal to or exceeding the nitrogen in the particulate matter at the beginning of the experiment. Where, as usually happened, the quantity exceeded that in the added diatoms and suspended particles, it may be inferred that the

excess was derived from organic nitrogen compounds in solution in the water. The ammonium set free changed to nitrite and subsequently to nitrate (Fig. 26), except under anaerobic conditions when the sequence stopped at the ammonium stage.

The rate of ammonium formation was about doubled for a rise of 6°–8° C., and in most experiments the subsequent oxidation to nitrite and nitrate was affected by temperature in a similar manner except at low temperatures in the region of 1°–2° C., when little or no change took place. In one experiment where water collected from a depth of 1200 metres was used, this

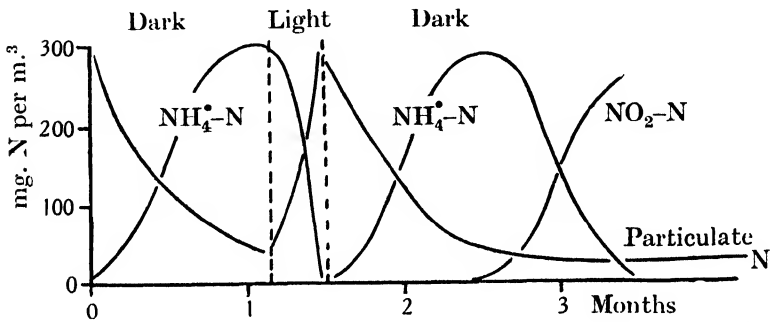

Fig. 27. Diagram showing the production of ammonium in sea water containing diatoms while stored in the dark, the utilization of this ammonium while kept in the light, and the subsequent production of ammonium and its conversion to nitrite in the dark. (After Von Brand & Rakestraw.)

subsequent oxidation was exceptionally slow, presumably due to the slow growth of nitrite- and nitrate-forming bacteria. It is of interest that ZoBell has observed that bacteria grow at different rates in waters collected from different positions and similarly enriched with nutrients, suggesting that sea water contains some growth-promoting factor or trace element affecting bacteria and that such occurs in variable quantity. A similar inference arises from experiments on the growth of diatoms (p. 140).

A series of experiments, in which diatoms were added at intervals to sea water stored in the dark, showed that after the second addition the production of ammonium nitrite and nitrate may take place simultaneously, the predominating product of bacterial action depending upon the dominance of ammonium-,

nitrite- or nitrate-forming bacteria which are present. In such water to which diatoms had been added and in which a flora had developed, the breakdown of diatoms added later was greatly hastened, and the concentration of ammonium formed from them in the water may remain quite low, being further oxidized almost as rapidly as it is produced. The step-by-step formation first of ammonium, then of nitrite, then of nitrate, may no longer be apparent if the later addition of diatoms is made during the stage of nitrate formation.

If the water to which diatoms had been added was stored in the dark until the ammonium maximum had been reached, or until any subsequent stage, then reinoculated with a few living diatoms and exposed to the light, all the ammonium nitrite or nitrate was used by the growing diatoms. Subsequent storage in the dark led to the regeneration of ammonium, followed by its conversion, step by step (Fig. 27). In this manner regeneration of organic nitrogen to nitrate, followed by its utilization, was repeated in the same culture three times. It is odd that the regeneration occurred step by step, there being a marked lag before nitrite and later nitrate formation took place, in spite of the rich flora of nitrate-forming bacteria present at the times of reinoculation.

In connection with these investigations Von Brand (1938) determined the organic nitrogen in particulate matter filtered from samples of sea water. He found only 5–18 mg. N per m^3 in the upper layers of the sea except where phytoplankton was very abundant, and in the deeper water below 300 m. no more than 1–3 mg. per m^3 at five positions in the open ocean.

The liberation of phosphorus in an available form was not followed in these experiments, but it presumably took place at the same time as ammonium formation, since there was enough there for the diatoms added as a reinoculation to grow (Fig. 27). However, there is no data of the quantity of phosphate in the water at the start of the experiments.

Dried diatoms when added to sea water were found by Waksman, Stokes & Butler (1937) to liberate two-thirds of their phosphorus as phosphate in 3 weeks at 22° C. Living diatoms were observed to be relatively resistant to bacterial decomposition until they have been attacked by protozoa. Cooper

(1935) stored sea water in the dark to which living diatoms had been added. After an initial lag period phosphate was liberated, but even after 3 months no more than two-thirds of the added organic phosphorus had appeared as phosphate.

Bacterial Oxidation of Ammonium to Nitrite and Nitrate

The various observations and experiments already mentioned indicate that bacteria which oxidize ammonium occur on plankton organisms, in bottom deposits and in the water immediately above the bottom, but that they do not occur freely suspended in the main body of the water away from land and away from immediate influence of the bottom.

There can be no doubt that the water close to the bottom is a site of active nitrification, particularly in waters of moderate depth. Experiments by ZoBell (1935*b*) indicate that nitrifying bacteria which had been isolated from bottom deposits were ideally suited to oxidize ammonia in the sea water but not within the deposits. It was found that the optimum oxidation-reduction potential for nitrification lay within 0·30 to 0·55 volt; the potential of sea water is *circa* 0·45 volt, due to the irreversible oxygen system (Cooper, 1937*b*), far removed from the low potentials found to exist in bottom deposits (ZoBell & Anderson, 1936*b*).

Fixation of Atmospheric Nitrogen

Bacteria of the aerobic *Azotobacter* species have been isolated by several observers and found attached to plant organisms, in bottom deposits and free in the water. The anaerobic *Clostridium* species has also been found in bottom deposits. Waksman, Hotchkiss & Carey (1933), who have isolated these bacteria from waters of the Gulf of Maine, conclude, after reviewing previous investigations, that the sea contains an abundant population capable of fixing appreciable quantities of nitrogen. They require a relatively rich supply of food. It still remains to be determined to what extent this process takes place in the sea, if at all.

Nitrogen-liberating Bacteria

Bacteria which are capable, under suitable culture conditions, of reducing nitrates and nitrites to nitrogen have been found in bottom deposits and in the sea by several observers. In order to set free gaseous nitrogen, they require readily available food as a source of energy and the presence of a relatively high concentration of nitrate; it is doubtful if these conditions are fulfilled in the oceans. A hypothesis, advanced by Brandt in 1899, that the quantity of nitrogen-containing salts in the sea was controlled by the activities of such bacteria, has received much attention. Subsequent considerations advanced by Gran, by Issatchenko and by Waksman lend no support to this hypothesis. Waksman, Hotchkiss & Carey (1933) have reviewed the various investigations on this subject. Thompson & Gilson (1937) quote experiments by Cranston & Lloyd on a bacterium isolated from the sea. These yielded results which can be explained by the assumption that nitrate was completely reduced to nitrite before the latter was reduced to hyponitrite, each stage being completed before the next stage commenced and before nitrogen was, finally, set free in the culture.

Nitrate-reducing Bacteria

In addition to true denitrifying bacteria which can reduce nitrate to atmospheric nitrogen, bacteria which are able to reduce nitrate to nitrite are abundant in the sea and in bottom deposits. In order to carry out this reduction, they also require a relatively rich supply of food. Waksman, Reuszer, Carey, Hotchkiss & Renn (1933) incubated a series of water samples from various positions and depths in the Atlantic after adding nitrate, phosphate and calcium acetate as source of food. Many but not all were found to produce nitrite.

Thompson & Gilson (1937) considered that the nitrite-rich layer occurring below the photosynthetic layer in the Indian Ocean was probably due to the reduction of nitrate through the agency of such bacteria. The later observations by Von Brand & Rakestraw, that dead diatoms yielded ammonia which was subsequently converted to nitrite and then nitrate, suggest that

this nitrite-rich layer may be due to nitrification by bacteria attached to plankton organisms, rather than to denitrification. It is perhaps pertinent that several observers have noted that nitrite is produced in cultures of diatoms growing in water rich in nitrate; ZoBell (1935) considers the possibility of extracellular reduction of nitrate by the plants. There is no clear evidence showing whether the nitrite in the nitrite-rich layer of the oceans is produced by nitrification of ammonium or denitrification of nitrate.

The reduction of nitrate to ammonium in the sea can be brought about by bacteria which utilize nitrate when their food supply is short of organic nitrogen and subsequently give off ammonium during autolysis. Whether there are species which bring about this reduction by another mechanism, denitrification, is open to some doubt (Waksman & Carey, 1935).

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IX. REGENERATION OF PHOSPHATE AND SALTS CONTAINING NITROGEN

The Phosphorus and Nitrogen Cycles

The rate at which phosphates and nitrogen compounds are utilized by plants, returned to the sea and again utilized, is a direct measure of productivity or fertility. Hence the cycle of events has received much attention, particularly the cycle which nitrogen compounds undergo.

Regeneration of phosphate

Orthophosphate in solution is utilized by phytoplankton and there is, as yet, no direct evidence that they obtain any of their phosphorus from dissolved organic phosphorus compounds in the sea, although this appears to be possible. Land plants have been found to absorb both phytin and lecithin as such through their roots (Rogers *et al.* 1940); the diatom *Nitzschia closterium* in bacteria-free culture is able to obtain all the phosphorus it requires for rapid growth from both phytin and glycerophosphate, growing more rapidly when supplied with phytin than when supplied with orthophosphate. (S. P. Chu, private communication.)

Phosphate which has been utilized to form part of the tissue of phytoplankton organisms is returned to the sea as phosphate in solution, following two main courses—direct and indirect.

There is reason to believe that the great majority of phytoplankton organisms are eaten by herbivores and these, in their turn, by carnivores. The animals excrete phosphorus as phosphate. Experiments by Gardiner (1937) showed that a herbivorous zooplankton organism, feeding on diatoms, excreted considerable quantities of phosphate into the water. In this way there is *direct regeneration* of some of the phosphorus in the plants, a regeneration which is relatively rapid. Much of it occurs within the photosynthetic zone; but not all, since many of the herbivores sink by day to depths below the zone, rising again at night.

Many species of the herbivorous zooplankton are exceedingly voracious, particularly when phytoplankton is abundant. They excrete great numbers of faecal pellets consisting of partly digested vegetable matter. It is probable that some of the phosphates which had been utilized by the plants is present within them as inorganic phosphate or very labile esters, which would dissolve into the water from these broken cells and be available at once for further plant growth.

In addition to this direct regeneration, large stable molecules of organic phosphorus compounds dissolve into the water from partly digested plants and dead animals, which are not again available until in course of time they are further decomposed. This cycle of events may be termed *indirect regeneration.*

Redfield, Smith & Ketchum (1937) have overcome the difficulty of estimating the organic phosphorus in sea water. By a method which embodies oxidation of the organic matter followed by reduction of the arsenate formed, they obtained a series of concordant observations at a position in the Atlantic on five occasions during the course of a year.

A marked increase in dissolved organic phosphorus occurred during the summer; between 5 and 16 mg. P per m^3 were then present in the upper layers, being three to four times more than is ever present in the organisms and organic detritus which was filtered from the water.

A subsequent decrease in the dissolved organic phosphorus in the whole water column indicated that most of it is regenerated as phosphate during the winter months.*

Various experiments and observations have been discussed concerning indirect regeneration due to the action of bacteria, also the liberation of phosphate into water to which mercuric chloride or chloroform had been added, presumably due to the action of enzymes in solution in the water. In addition to such

* The occurrence of phosphorus in solution in a freshwater lake is of interest to compare with conditions in the sea. Hutchinson (*Ecol. Monog.* **11**, 21, 1941) records 10–20 mg. P per m^3 during the summer months, increasing during the autumn, in the upper layers of water. The phosphorus consisted on the average of

29 % in solution as organic phosphorus,
8 % in solution as inorganic phosphorus,
63 % in particulate matter, being largely particles of ferric phosphate.

changes there is also the possibility that direct oxidation or hydrolysis takes place in water. Cooper (1937) suggests that the high phosphate concentrations occasionally found at the surface may be due to direct oxidation caused by the forces which exist at the air-water interface.

When compared with excretion of phosphate by animals, indirect regeneration is not only a slow process but much of it takes place below the photosynthetic zone. A very long period of time may then elapse before it is again within the zone and once more available.

Phosphate from rivers

With regard to the accretion of phosphate other than from marine organisms, the coastal areas of the sea are enriched with phosphorus and nitrogen compounds carried down by rivers and streams. During the summer months the phosphates and nitrogenous salts are largely used up by plant growth in the non-tidal

TABLE 16. *Milligrams of phosphate-P per cubic metre in the surface water at varying distances offshore*

Date	In Plymouth Sound	2 miles offshore from entrance to Sound	10 miles offshore	19 miles offshore
Sept. 13, 1923	10·5	8	4	0
Oct. 15	5	7·5	6·5	9·5
Jan. 2, 1924	10	14	16	16·5
Feb. 15	15·5	13	15·5	14
June 17	1·5	1	1·5	1
July 9	1·5	1	0	1
Aug. 7	6	3·5	0·5	0·5
Sept. 3	12	12	6·5	5
Nov. 12	8	9	14·5	6
Dec. 9	15·5	15·5	14·5	14

and tidal parts of the rivers before reaching the open sea (Atkins, 1925). Even during winter, when the rivers do carry down considerable quantities, their effect is not apparent beyond a limited distance from the shore (Table 16). Even with a great river such as the Mississippi, discharging some 50 tons of phos-

phorus daily, Riley's (1937) observations indicate that its effect is not clearly apparent beyond some 90 miles offshore. In general the phosphate content of fresh waters is not high, and does not often exceed 5 to 10 mg. phosphate-P per m^3 unless much polluted with urine.

Regeneration of salts containing nitrogen

The cycle of changes which nitrogen compounds undergo in the sea is more complicated than that of phosphorus compounds. Phytoplankton can utilize a variety of nitrogen compounds; marine animals excrete several into the sea; there are bacteria present capable of reversing the later stages of degradation from ammonia to nitrite to nitrate; there are bacteria capable of both fixing and setting free atmospheric nitrogen; direct oxidation, at least of ammonium, can take place through the agency of activators other than bacteria.

Planktonic diatoms are able to utilize nitrate, nitrite and ammonium, also urea and uric acid. It is not surprising that they readily utilize urea, since in sea water this is partly dissociated into ammonium and cyanate ions; Cooper (1937) has computed the equilibrium constant, which indicates that it is mostly dissociated in sea water. Planktonic diatoms with their associated bacteria readily de-aminate some amino-acids, but appear unable to use others (Harvey, 1940). They also appear unable to use trimethylamine oxide. Schreiber (1927) found that bacteria-free cultures of *Carteria*, a marine flagellate plant, could utilize glycine. Braarud & Foyn (1930) found that similar cultures of *Chlamydomonas* could utilize glycine, alanine and asparagine.

Marine animals excrete nitrogen largely as ammonium, and also as urea, uric acid, trimethylamine oxide and amino-acids. Baldwin (1937) cites analyses of the excreta of several marine animals. It therefore appears that, when plants are eaten by animals, most of the nitrogenous organic matter, which is digested, undergoes *direct regeneration* into compounds which can be again utilized by plants without further breakdown. The excretion taking place within the photosynthetic layer is, moreover, immediately available.

Investigations concerned with the action of bacteria, and of enzymes in solution, in setting free ammonium from nitrogenous organic matter, either in solution or particles, and the subsequent autolysis of the bacterial tissue have been discussed (Ch. 8). This constitutes the relatively slow process of *indirect regeneration*. It is noteworthy that the sea contains only a small store of organic nitrogen present in organisms and detritus, Von Brand's estimations indicating that only a few milligrams of organic nitrogen per cubic metre are usually present in this form (p. 111), whereas one hundred milligrams or more are often present in organic matter in solution (p. 39).

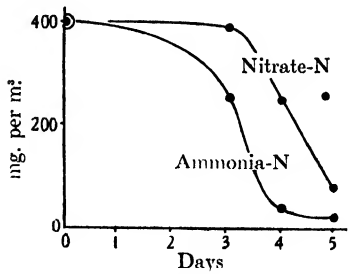

FIG. 28. Preferential utilization of ammonium. Diagram showing the fall in concentration of ammonium and nitrate due to utilization by phytoplankton from a sea water containing initially 400 mg. per m³ of ammonium-N plus 400 mg. per m³ of nitrate-N.

Oxidation of ammonium, and interconversion of the products, which may take place subsequent to the formation of ammonium, probably have no effect upon the production of plant life in the sea. Indeed, experiments show that phytoplankton diatoms utilize ammonium in preference to nitrate (Fig. 28). In the presence of sixty times more nitrate than ammonium-nitrogen, an experiment showed that most of the latter was absorbed before there was any appreciable utilization of the nitrate by the diatoms (Harvey, 1940).

A suggestion has been made by Cooper (1937) that direct oxidation of organic compounds with the production of ammonia may occur at the surface of the sea, particularly where bubbles abound and a large surface is presented in contact with the air. Many chemical reactions are activated at interfaces, and on many occasions more ammonium has been observed at the surface than in the water immediately below.

With regard to the oxidation of ammonia, activated by bacteria or enzymes, and the interconversion of the products

$$NH_4 \rightleftharpoons {}''N_2O_2 \rightleftharpoons {}'NO_2 \rightleftharpoons {}'NO_3,$$

Cooper (1937) has presented evidence for the intermediate

formation of hyponitrite. The oxidation to nitrite is also brought about by ultra-violet light (ZoBell, 1933; Rakestraw & Hollaender, 1936). However, as sunlight penetrates the sea, the ultra-violet waves are rapidly scattered and absorbed (Atkins, 1932). Hence it is not likely that photochemical oxidation plays any large part in nature.

Oxidation of ammonium to nitrite in sunlight does not occur in distilled water, artificial sea water, or in sea water which has been autoclaved at 120° C. Cooper (1937) makes the interesting suggestion that photochemical oxidation in sea water may be sensitized by colloidal silica in solution, and that heating to 120° C. aggregates the colloid, rendering it inactive. It had been observed that silica sensitized the reaction in tropical soil waters.

Combined nitrogen from rivers and rain

The sea receives a small annual addition of combined nitrogen from river water and rain. Clarke (1924) estimates that rain brings some 28 mg. of nitric-nitrogen and 56 to 240 mg. of ammonium-nitrogen to each square metre of the sea surface annually. Deacon (1933) found 10 mg. of nitric-nitrogen per m^3 of tropical rain, Braarud & Klem (1931) 24 to 34 mg. per m^3 in snow on the coast of Norway. Braadlie (1930) has determined the nitric- and ammonium-nitrogen in rain and snow throughout the year on the Norwegian coast, finding an average of some 135 mg. NH_4-N and 75 mg. nitric-N per m^3.

The quantity of combined nitrogen discharged into the sea by rivers is much less during summer than winter. The annual addition to the sea from land drainage is considerable, but compared with the store of combined nitrogen in sea water this addition must be very small indeed. Riley (1937) quotes analyses showing Mississippi water to contain on the average throughout the year:

NH_4-N	20 mg. per m^3	Nitrite-N	5 mg. per m^3
Albuminoid-N	350 ,, ,,	Nitrate-N	200 ,, ,,

Sea water, except in the upper layers where plant growth is taking place, contains about half this quantity of combined nitrogen.

Bacterial fixation of dissolved nitrogen by *Azotobacter* and *Clostridium*, in the water, on plant organisms, and in bottom deposits, has not been demonstrated to take place in nature.

There may be some small annual loss of combined nitrogen through the agency of denitrifying bacteria, but no evidence has been found indicating that this takes place, with the possible exception of a few inshore positions where there is a deposition of organic matter on the bottom and a considerable concentration of nitrate in the water.

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X. THE FERTILITY OF OCEAN WATERS

PREVIOUS chapters have been largely devoted to changes in the constituents of sea water brought about through the agency of plants and animals. There remains to consider the converse, how changes in these constituents, and in physical conditions, affect the growth of plants and animals; how the waters control the fertility of the seas. The productivity of any extensive water mass has been defined as the quantity of organic matter produced by the phytoplankton over a period of time, such as a year. This organic matter provides animals and bacteria with food; its quantity is dependent upon the number of times during the year that plant organisms are produced, consumed, and their nitrogen and phosphorus set free in a form and at a depth where they can again be used by the phytoplankton to synthesize organic matter.

Any study concerning productivity necessitates the comparison of one area with another and involves comparison of quantities. The first is complicated by the constant movement of the water occupying an area, its slow replacement by a different body of water, and often the more rapid replacement of the upper layers. The comparison of quantities involves sampling over wide areas, usually to considerable depths, of animals and plants frequently distributed in swarms or patches. To complicate matters further, there is a production of minute plant organisms, no more than a few μ in size, in some areas at some periods of the year.

The standing crop of phytoplankton, or breeding stock, at any time is merely a 'momentary balance' between the processes of production and of consumption by animals and bacteria. The concentration of nutrient salts in the water mass at any time is likewise a momentary balance between their regeneration by animals and bacteria and their consumption by the phytoplankton.

The quantity of organic matter produced during any extended period of time is dependent upon a series of conditions many of which are themselves closely interrelated. In comparing two

different water masses, a smaller average standing crop of plants and lower concentration of nutrient salts does not *necessarily* mean a smaller production of organic matter if other conditions, such as light and temperature, allow more rapid growth of the plants or growth which extends to greater depths, or if, when consumed, their contained nitrogen and phosphorus are more quickly regenerated within the photosynthetic zone in forms which can be again utilized, or alternatively soon brought by turbulence into the zone from below.

The assessment of the annual production of plant organisms does not lend itself to direct attack, but a consideration of the factors involved is beginning to shed light upon its magnitude. It is generally assumed that, in water masses where the annual production is great, the density of the animal population will be great; this assumption is roughly borne out by general observation. A series of quantitative observations are now indicating a relation between the fluctuations in production from year to year and the animal population.

With these considerations in view it is of interest to discuss factors which affect, or may affect, the growth rate of phytoplankton in the sea and at times slow down growth and so limit production. The list is probably still incomplete. Most of the factors are interrelated, and some have an optimum value beyond which production is hindered. It is the mosaic of such factors, constantly changing, which controls production in nature.

The Effect of Light, Temperature and Turbulence on the Growth of Phytoplankton

The light falling on the sea is continuously changing with time, and as it penetrates the water it changes rapidly in spectral composition. In the clear blue water of the open ocean—containing the least suspended matter and organisms—the blue and blue-green penetrate deepest. As shores are approached and more suspended particles are encountered in the water there is, in addition, a progressively greater loss due to scattering of light by these particles, particularly of light at the blue end of the spectrum. In a turbid estuary the loss from this cause becomes so great that blue light penetrates less deep than that from the

red end of the spectrum. The change in composition is reversed (Cooper & Milne, 1938, 1939). Differences in transparency of the sea have a particularly great effect on the depth to which light penetrates and the composition of the light at successive depths. It is noteworthy that in the transparent water of the Mediterranean sessile algae obtain sufficient light to live at depths exceeding 100 metres; experiment with a diatom culture in the Sargasso Sea indicated considerable photosynthesis taking place below 100 metres during daylight (Clarke, 1936). In the less transparent waters of temperate seas the photosynthetic zone is very much shallower.

With daylight the intensity of any one group of wave-lengths is roughly proportional to the intensity of all the groups in the whole spectrum. Hence the intensity of the whole spectrum can be measured by a photoelectric cell sensitive to a particular group of wave-lengths which has been calibrated against a standard light source. The value of the intensity (usually expressed in metre-candles or lux) is a function not only of the intensities of the groups of wave-lengths which make up the spectrum of daylight but also of the group of wave-lengths to which the particular photoelectric cell is sensitive and of the occurrence of this group in the particular light source against which it has been calibrated. Photometer readings therefore may not always give a directly proportional comparison between daylight and artificial light or daylight which has penetrated to a depth in the sea and changed in spectral composition.

These considerations delineate the value of experiments on the growth of phytoplankton in artificial light and indicate some of the complications involved in interpreting observations made in the sea.

With regard to the utilization by phytoplankton of light of different wave-lengths there is a dearth of information. Stanbury (1931) grew a marine diatom in daylight which had passed various coloured light filters and found that growth was not proportional to the percentages of the total incident daylight which passed through the filters (the intensity of the light reaching the diatoms) but was more nearly proportional to the amount of light energy which reached them. The energy is a function of intensity and spectral composition of the light.

A number of investigations have been made concerning the

range of light intensity necessary for the growth of phytoplankton and concerning their growth rate at varying depths in the sea, both for short periods and over a period of 24 hours, during days in summer and winter.

Gaarder & Gran (1927) kept a mixed community of diatoms, freed as far as possible from animals, in flasks hung at different depths in Oslo Fiord in March. Below about 10 metres—the compensation point—their respiration exceeded assimilation. Marshall & Orr (1928) made similar experiments with a culture of the diatom *Coscinosira polychorda* in Loch Striven, finding that the compensation point over 24 hours lay between 20 and 30 metres deep in summer and near the surface in winter. Close to the surface growth was inhibited during the hours of bright light in summer. Similar results were also obtained with a summer species of *Chaetoceros*. They noted that optimum growth took place throughout a *range* of a few metres, below which it decreased until the compensation point was reached.

Similar experiments were made by Jenkin (1937) in the English Channel using a culture of the diatom *Coscinodiscus excentricus*. Over 24 hours in the summer greatest growth took place between $2\frac{1}{2}$ and 10 metres depth, the compensation point in this more transparent water lying at about 45 metres. Photometer measurements at different depths were made during the course of these experiments and from them the flux of light energy was calculated. The oxygen production by the diatoms showed a linear relation to the flow of light energy through the water when this was between 7·5 joules (or 1·8 g.cal. per cm^2 per hour) and the compensation point (0·55 joule). Above 7·5 joules the linear relation ceased. In the shorter-period experiments maximum oxygen production occurred in a range between about 12 and 30 joules per cm^2 per hour, and at greater intensities inhibition became apparent, actual contraction of the chloroplasts probably taking place at an energy flux of some 40 joules per cm^2 per minute. In the region of the optimum there were marked differences between the various experiments. Additional experiments with *Biddulphia regia* gave similar results. Other investigators have determined the light intensity at the compensation point, obtaining photometer measurements of 100 to 500 lux, in rough agreement with the value of 0·55 joule per cm^2 per hour which is equivalent to about 360 lux of daylight.

A phenomenon which seems to lack explanation is the time at which phytoplankton start to increase rapidly at the beginning of the year. In temperate seas a considerable concentration of nitrates and phosphates, and presumably of all other constituents necessary for plant growth, is found in the upper layers before midwinter. The stage is set for rapid growth and the production of a large standing crop, but something less obvious than sufficient light seems to be necessary before the spring outburst of diatoms takes place. In the deep waters of the Gulf of Maine in latitude 41° to 43° N. at 2° to 3° C. it occurs no earlier than in latitude 63° N. in the deep water off the Norwegian coast at 4° to 5° C., nor in the relatively shallow water of the English Channel at some 8° C. in latitude 50° N. In some parts of the Gulf it may occur no earlier than in water of the Barents Sea at $-1°$ C. in latitude 73° N.

In the region of the Gulf of Maine considerable growth is recorded in December–January at Woods Hole and Cape Cod Bay, but in the deeper offshore waters this does not happen until March–April, there being as much as six weeks' difference between various parts of the open Gulf (Bigelow, Lillick & Sears, 1940). It occurs over Georges Bank before it takes place in the deep water around; Riley (1941, 1942) points out that loss of breeding stock in the photosynthetic zone will be greater during storms in deep water, since turbulence will carry some of the plants to greater depths than is possible over the bank. A well-marked correlation was found between the turbulence and the date when spring growth started at several positions in this area. A similar explanation of growth taking place over the Faeroe Bank before it takes place in the surrounding deep water has been advanced by Steeman Nielsen (1935).

Off the Norwegian coast, Braarud & Klem (1931) observe the spring outburst to occur first in the sheltered waters of the fiords and in the deep water beyond the shelf which extends some 20 miles seaward. Over the shelf growth starts later.

In the Arctic, Kreps & Verjbinskaya (1930) have found a considerable growth of phytoplankton taking place early in May in Atlantic water at $-1°$ C. in latitude 73° N., whereas farther south in water of $+1{\cdot}5°$ C. of Arctic origin in latitude 70° to $71\frac{1}{2}°$ N. growth did not start until later.

It is remarkable that the spring outburst was taking place in early May in 73° N., while Bigelow, Lillick & Sears (1940, p. 159) consider that it may be expected about the same time in the northern part of the western basin of the Gulf of Maine, in 43° N.

In the southern hemisphere, Dakin & Colefax (1940) note that the spring increase occurs at about the same time off the east coast of Australia in 34° S. as off the Californian coast in 36° N. latitude.

Between latitudes 50° and 70° S. in the Antarctic, the standing crop increases rapidly to a maximum, starting about 3 weeks before midsummer (mid-December) in the more northerly latitudes and not before midsummer in the more southerly latitudes. However, off South Georgia and in the Scotia Sea the inception is some 3 weeks earlier than in the same latitude away from the influence of land (Hart, 1941).

These considerations suggest unrecognized factors controlling the inception of growth in some areas. The subsequent decline in the standing crop may be due to grazing in some areas; it occurs at a time when herbivores are increasing rapidly and is often associated with great numbers of faecal pellets in the water. Doubtless the intensity of grazing and the hindering effect of turbulence affect the inception of the spring outburst, but there is no evidence that they account for all the anomalies which have been mentioned.

It is noticeable when growing diatoms in culture that their behaviour and growth rate depend to a large extent upon their previous history, whether they have been making rapid or slow growth before being introduced into the culture medium, that is to say upon their 'physiological state'.* The following experi-

* It seems likely that, in nature, the 'physiological state' of the plant cells may at times so affect their growth rate as to override the physical and chemical conditions of their environment. It has for long past been an outstanding problem to account for the sequences of species which occur in the sea; the plant life may consist almost exclusively of one species of diatom which increases in population density for a period of some weeks, then, quite suddenly, the cells of this dominant species sink and their place is taken by another rapid growing species, often without any lag in time, and without any obvious reason, such as a sudden change in physical or chemical conditions. Recent observations by Tutin and Storey in Lake Windermere suggest that diatoms in their natural habitat—sub-optimal concentration of their nutrient requirements—arrive at a 'physiological state' when they are no longer capable of growth. Diatoms transferred to a culture medium at intervals during the waxing population

ment (Harvey, 1939) shows both this and the effect of temperature on growth rate. A culture of *Biddulphia mobiliensis* was divided into two parts. One was then grown in a north window in relatively dim December light. The other portion was grown near an electric bulb immersed in a bowl of running water; it received continuous light of some 18,000 lux measured with a photometer. At the end of a week subcultures of each of these cultures were made in sea water enriched to the same extent. Each subculture was divided into ten glass vessels. They were immersed in two water-baths, one kept at 13° C., the other at 18° C., at different distances from an electric bulb which was immersed in each bath. The light which each vessel of culture received was measured. After 72 hours' continuous light the percentage increase in number of cells which had taken place during the 72 hours was determined.

	Temp. ° C.	Percentage increase in cells after 72 hours in				
		28,000 lux	18,000 lux	8000 lux	4100 lux	1400 lux
Cells grown previously in dim light	18	7	68	66	106	87
	13	24	16	14	8	2
Cells grown previously in continuous light at 18,000 lux	18	171	236	190	123	98
	13	31	70	105	67	36

Barker (1935) has investigated the effect of temperature on two species of the diatom *Nitzschia* and several dinoflagellates. The optimum varied for the different species; below the optimum there was a roughly linear relation between temperature and growth rate.

These various observations indicate that phytoplankton has sufficient light to make active growth down to a depth of more than 100 metres in the clear blue transparent waters of the open sea in summer or tropic light; as the shores are approached this photosynthetic zone rapidly shallows, and in estuaries may be no more than a few metres deep. During the short days of

of this species in the lake grew readily in the culture medium. However, at the time when this species had reached its maximum population in the lake or had started to wane, they did not grow when transferred to the culture medium. Plants which had been transferred to the culture medium immediately prior to this climacteric continued to grow and make many divisions.

midwinter in temperate regions the quantity of light energy entering the sea daily is only a fraction of that entering daily in the summer, about one-ninth in the English Channel area (Atkins, 1939). It does not follow that the quantity of light available for photosynthesis in the sea is nine times less in winter than in summer. At this position about one-half of the blue light entering the surface penetrates to a depth of 5 metres, and one-ninth to a depth of some 16 metres. Thus the photosynthetic zone averaging 45 metres deep for the 24 hours in summer would shallow and average some 16 metres in winter—still sufficient for considerable growth to take place. Considerable growths during winter in temperate seas are unusual but they have been observed in relatively shallow waters. Thus Bigelow (1926, p. 396) and Fish (1925) have reported heavy growths of diatoms during December in Cape Cod Bay and at Woods Hole.

In nature there is yet another physical factor besides light and temperature which obviously affects production. Vertical mixing of the water is continuously taking place through turbulence or eddy motion. This has a dual effect, increasing or hindering the growth of plants. Without it the photosynthetic zone would soon be depleted of nutrient salts except in shallow areas and life would cease through lack of supplies from below. Incidentally the whole physical state of the oceans and the world's climate would change, the viscosity of the water becoming laminar.

Such eddy motion or turbulence is set up by wave motion, by cooling and evaporation at the surface causing convection currents, and also by a current meeting even a low submarine ridge or bank. The freedom of the eddy motion to penetrate from the surface downwards is reduced where the density of the water increases with depth, that is, with increasing 'stability' of the water column. Unfortunately, the amount or degree of turbulence (coefficient of eddy diffusion) rarely lends itself to direct measurement in the sea.*

* The vertical component of *eddy diffusion* has been computed by a number of observers. The coefficient A (or Austausch) is defined by

$$\frac{dQ}{dt} = A \frac{dc}{dn},$$

where Q is the quantity in grams of some constituent of the water, such as chloride or phosphate or heat, which passes a horizontal surface of 1 sq. cm.

There are some areas where the effect of turbulence bringing nutrient salts into the photosynthetic zone is reinforced by water upwelling from below to take the place of surface layers which are being drawn away in a current. This is particularly well marked in two areas off the tropical west coast of Africa, where the plankton is singularly abundant (Hentschel & Wattenberg, 1930), and off the west coast of South America (Gunther, 1936).

With regard to turbulence hindering production, plant organisms are continuously being carried down from the levels where they are making most rapid growth, and if carried below the photosynthetic zone are then lost to the breeding stock and furthermore lose substance through respiration. The losses from respiration will presumably deplete the food reserves, mostly fatty acids, and may increase the specific gravity of the plants if they have remained for a period below the zone.

This continuous drain on the rapidly breeding plants is likely to be most where the turbulence is greatest and the photosynthetic zone shallow, with a great depth of water below it.

Marked diminution in production has been attributed to this factor in the Bay of Fundy by Gran & Braarud (1935) and in deep Antarctic waters by Hart (1934). In these areas there is always an ample supply of nutrient salts in the upper layers.

In many shallow areas turbulence also acts indirectly in hindering plant growth by rendering the water turbid with detritus brought up from the bottom and kept in suspension. This is marked in the Bay of Fundy, in the immediate vicinity of South Georgia (Hart, 1934) and indeed in most shallow areas where there are strong tidal currents.

It seems probable that turbulence plays a large part in limiting production, particularly during the winter in all temperate seas.

in 1 second, dc/ds being the concentration gradient of that constituent in grams per c.c. per cm. in a vertical direction at this surface.

The computed values vary from 0·02 to 0·6 for waters changing rapidly in density with increasing depth in the Baltic to 320 for homogeneous waters in the Atlantic. The majority of computations lie between 2 and 90.

Computations have also been made of the horizontal component of eddy diffusion, giving values of 10^6 to 10^8.

Thus a condition for greatest production occurs in the sea where the relation of turbulence to the quantity of incident light is at an optimum.

The Effect of Concentration of Nutrient Salts on the Growth Rate of Phytoplankton

In nature the growth of phytoplankton frequently reduces the concentration of phosphate to below 1 mg. per m^3, and the concentration of available nitrogen compounds—nitrate, nitrite, ammonium, uric acid, urea and probably amino-acids—to a small value. Hence it is pertinent to consider how the approach to low concentrations affects the rate of growth.

Experiments with the diatom *Nitzschia closterium* have shown a marked reduction in rate of photosynthesis with phosphate concentrations below about 10 mg. P per m^3, most marked below 5 mg. P per m^3 (Harvey, 1933). Ketchum (1939*a*), using the same species, has concluded that the rate of growth is independent of phosphate concentrations above 17 mg. P per m^3, below which it falls off. In water with ample phosphate the rate of division was independent of nitrate concentrations above 47 mg. N per m^3, the lowest concentration examined.

The same author (1939*b*) has found that, when this diatom is grown in a medium lacking phosphate, phosphorus-deficient cells are formed. These absorbed phosphate in the dark when phosphate was added. The alga *Chlorella pyrenoidosa* when grown in a medium lacking nutrient salts formed cells containing only a third of the normal phosphorus and half the normal nitrogen. This suggests that in nature utilization of nutrient salts from water having very low concentrations may proceed continuously, while carbon assimilation takes place only during daylight. Such a mechanism allows growth at greater dilutions of nutrients than would otherwise be possible, and the most efficient use of short periods of illumination in waters depleted of nutrient salts.

The observation, that algae form phosphorus and nitrogen-deficient cells when illuminated in media so low in either nutrient that they cannot absorb sufficient to keep pace with carbon assimilation, suggests that under these circumstances they may attain a larger proportion of fat to protein than when living in

plenty. The analyses made by Clark & Mazur (1941) of the lipid content of diatoms net-caught in the Gulf of Maine, in conjunction with the sparse existing data on the carbon-nitrogen and the ash-organic matter ratio in marine diatoms, suggest that these plants normally contain rather more protein than lipid—this lipid being mostly free fatty acids with a small proportion of fat and hydrocarbons. It has been noted that when diatoms are grown in culture they often contain many refractive fatty globules, such as stain with Sudan red, when their growth is slowing down or ceasing due to exhaustion of a nutrient.

The growth rate of plants is reduced by low concentrations of nutrient salts in solution in the water in many areas of the sea, but there is no reason to suppose it is ever brought to a standstill since both phosphate and available nitrogen compounds are continuously being reformed. Analyses have shown the phosphate concentration to be sometimes reduced to less than 0·5 mg. P per m^3, with a small concentration of nitrate + nitrite; at other times and places the latter have been found at less than 1 mg. N per m^3 with a small concentration of phosphate. This latter condition does not necessarily mean that the final limit has been brought about by lack of available nitrogen because it is possible and indeed likely that the water contained ammonium and amino-acids. Experiments with plankton diatoms grown in water to which both nitrate and ammonium had been added showed that they utilized ammonium in preference to nitrate (Harvey, 1940). Indeed, it appears doubtful whether the change of ammonium to nitrite and nitrate, which takes place in nature, plays any part in influencing the productivity of the sea or the kind of plants and animals in it.

The concentrations of nutrient salts change together in the sea, the ratio of phosphate to nitrate + nitrite remaining within fairly narrow limits over very wide areas. For this reason the concentration of phosphate usually affords a close index of the concentration of both nutrients in the water. There are, however, some water masses where the ratio of N to P differs considerably from the customary value of 9 to 1 by weight, which is also the ratio in which the two elements tend to be present in phytoplankton organisms.

In temperate and Arctic seas plant life is at a minimum during the winter months, and incidentally the zooplankton is also at a minimum, there being a great diminution during the autumn. Towards the end of the winter a maximum of both phosphate and nitrogen salts, by that time mostly nitrate, become accumulated in the water and tolerably well distributed from top to bottom owing to vertical mixing brought about by cooling at the surface and consequent convection currents. The magnitude of this 'winter phosphate maximum' is of particular interest since it has been found to fluctuate from year to year in the same area.

Phosphorus occurs in the sea in three forms: as phosphate in solution, as organic compounds in solution, and in plants, animals and detritus. At the time of the winter maximum the investigations of Redfield *et al.* (1937) indicate that the quantities present in organic compounds in solution and in living animals and detritus are both much reduced.

Percentage of total phosphorus in upper 60 metres of the Gulf of Maine

	Aug. 20	Feb. 26
Phosphate	61·2	89·5
Organic phosphorus compounds in solution	30·1	6 4
Organisms and detritus	8·7	4·1
	100	100

Production in the sea is slowed when the *concentration* of nutrient salts falls to low values, but it is the *rate of replenishment* of the nutrients in the water of the photosynthetic zone which ultimately limits the production. The quantity of nutrients in the photosynthetic zone—a momentary balance between utilization and replenishment—is a measure of the potential production in the immediate future. There are good grounds for supposing that this quantity is used and used again, perhaps several times during the course of a year, in forming plant tissue. Hence it is the rate of replenishment which ultimately controls production.

The Supply of Iron, Silicates and Carbon Dioxide to Phytoplankton

There are grounds for expecting that the growth of phytoplankton may be limited in some parts of the open oceans by an insufficient supply of iron. Only a few milligrams per cubic metre can be found by analysis in sea water. Seiwell (1935) could detect none in the upper 40 metres' layer at a position in the Atlantic by a method which would detect 1 to 2 mg. per m^3. Cooper (1937) concluded that less than 10^{-7} mg. of iron ions per m^3 could exist in sea water in equilibrium with ferric hydroxide, owing to the insolubility of the latter. It is probable that most of the small amount of iron in solution exists as colloidal micelles of ferric hydroxide and possibly ferric phosphate (Harvey, 1937).

Phytoplankton organisms yield on analysis relatively large amounts of iron, several times more than their phosphorus content (Cooper, 1935), very much more than they could obtain from iron ions in solution. There is evidence that most of this is in the form of ferric hydroxide, and possibly ferric phosphate, adsorbed on the surface of the organisms (Harvey, 1937).

Experiment with diatoms in culture has shown that they are able to obtain their requirement for growth when this is added in the form of particulate ferric hydroxide, from which it may be concluded that they possess some mechanism for dealing with the extremely insoluble hydroxide at the cell-water surface. The actual quantity of iron required *within* the cell is probably very small; experiment with cultures showed that the addition of 1 mg. of iron to an iron-deficient medium led to a growth similar to that brought about by the addition of 175 mg. phosphate-phosphorus to a phosphorus-deficient medium, provided that the addition was made as recently formed colloidal hydroxide (Harvey, 1937). The inference is drawn from these observations that a fraction of a milligram of iron per m^3 in the sea should suffice for phytoplankton growth, provided this is present as small colloidal micelles of the hydroxide such as are formed when many organic compounds of iron hydrolyse at great dilution in sea water. The rate at which these aggregate to form larger micelles and the nature of the iron voided into the water

when phytoplankton is eaten by animals must both play a part, for it is the particle size of the iron hydroxide in the water, as much as its concentration, which is likely to determine whether a water is deficient in this element.

The colloidal ferric hydroxide, formed in sea water when iron salts hydrolyse at great dilutions in the presence of polyhydroxy organic compounds, obtains a considerable measure of protection from aggregation due to the influence of the organic compound. Of many iron salts of polyhydroxy anions examined, ferric ascorbate, the salt of vitamin C, hydrolysed to the least unstable colloidal hydroxide. Such 'protection' of the colloidal hydroxide doubtless plays an important part in reducing aggregation and flocculation in nature.

The total iron found by analyses of various sea waters, considered in relation to the high ratio of iron to phosphorus in analyses of diatoms, indicates that all the iron in offshore water is collected by phytoplankton organisms several times during the year. Colloidal ferric hydroxide is readily adsorbed on many organic surfaces, not only phytoplankton organisms. It would seem likely that the sequence of events which maintains the presence of colloidal ferric hydroxide in the upper layers of the oceans beyond the influence of land drainage follows a course such as adsorption of the hydroxide on the surface of plankton organisms which, on being eaten and digested, is redissolved and voided into the sea as a ferric salt together with soluble or colloidal organic matter; as this mixes with the alkaline sea water ferric hydroxide is formed from these iron salts, and this is 'protected' from aggregation and flocculation by the organic matter voided with the salts. Unless there is some such cycle of events it is difficult to understand why the upper layers would not become depleted of iron within a few years or less.

The silicate present in sea water can be estimated down to concentrations of about 10 to 15 mg. SiO_2 per m^3. The utilization of silica by diatoms occasionally reduces the silicate content of the upper layers of the sea to such a value. There is no evidence at what concentration the growth rate of diatoms is slowed through a short supply of silica. In the English Channel, some 4 miles offshore, Cooper (1933) finds the silica content of the water reduced from a winter value of 300 mg. SiO_2 per m^3 to

100 mg. by the end of April, after which it rises. At this position considerable and rapid growths of diatoms occur during May and June; later, as in most north temperate latitudes, the diatom community gives way to a flora in which peridinians with chitinous skeletons predominate. The rapid increase in silicate which occurs during the summer shows that it is quickly regenerated by solution of diatom frustules, or by solution of detritus in suspension.

Hart (1934, 1941) and Clowes (1938) consider that short supply of silica slows the rate of diatom growth in the Antarctic, where concentrations fall from some 2000 mg. SiO_2 per m^3 to very low values in some areas during the summer. Thin-walled diatoms occur at this time, and there is a correlation between the silicate content of the water and the silicification of the diatom *Corethron*.

There is an abundant supply of carbon dioxide in the sea, mostly in the form of bicarbonate. In the surface layers it exerts a partial pressure of the gas similar to its partial pressure in the atmosphere (p. 72). However, an outburst of phytoplankton sometimes occurs, utilizing 1·5 to 3 c.c. of carbon dioxide per litre of water, raising the *p*H of the water by *circa* 0·15 to 0·2. Such a change may lower the partial pressure of the gas by as much as 50 %. In view of this large effect it is pertinent to consider the relation between the supply or partial pressure and the growth rate of phytoplankton.

Barker (1935) investigated the rate of photosynthesis of a fresh-water diatom and of a unicellular alga in relation to the partial pressure of carbon dioxide, finding little difference unless the pressure fell below about one-quarter of its value in the atmosphere. Experiments with the marine diatom *Nitzschia closterium* in waters of different hydrogen-ion concentration indicate that there is an ample partial pressure of carbon dioxide for photosynthesis to proceed at or near the maximum rate in waters likely to be met with in the open sea (Harvey, 1933; Barker, 1935). This species and some others continue to live and multiply in cultures which attain a singularly high *p*H, whereas the majority of planktonic species die out under such extreme conditions (Harvey, 1940). Nevertheless, these planktonic species live and multiply in culture using carbon dioxide when its partial pressure can be only a small fraction of the value likely

to occur in the open sea. These various observations provide no indication that growth is materially affected by low partial pressure of carbon dioxide in the sea, where the *p*H rarely exceeds 8·35.

On the other hand, in culture, it is only some species, such as *Nitzschia* and other 'aquarium forms', which persist if the *p*H rises above about 9 to 9·5. The great majority of planktonic species found in the sea die out under these conditions of high *p*H and extremely low partial pressure of carbon dioxide. However, when fresh samples of sea water were enriched with nitrate, phosphate and iron, kept in a north window with a stream of air bubbling through them and shaded when necessary to keep the *p*H below 9, cultures of diatoms resulted and these were substantially the same communities of species as were present when the waters had been collected. In this manner growths were obtained which had utilized 200 mg. phosphate-phosphorus per m^3 and nine times this amount of nitrate-nitrogen.

The Effect of other Minor Constituents of Sea Water on the Growth of Phytoplankton

Experiments have been made with the diatom *Ditylum brightwelli*, growing it in water collected from the open sea which had been heated to 90° C. and enriched with phosphate, nitrate and iron. In some samples of water treated in this manner consistently good growth of the diatoms was obtained. In some samples, the diatoms with which the waters were inseminated formed auxospores and ceased growth unless a small quantity of *manganese* was added, from 1 to 2 mg. per m^3 being sufficient. In other samples the growth rate of this species and of *Thalassiosira gravida* was materially increased by adding manganese, provided that the intensity of illumination was low or reduced to a few hours daily. Analyses of water from the Pacific by Thompson & Wilson (1935) show it to contain a variable small quantity of manganese, ranging between 1 and 10 mg. per m^3, so it is possible that lack of manganese may play some part in nature.

No growth, or only very slight growth, of *Ditylum* was obtained in a series of samples of water collected during the

summer months unless some compound containing divalent sulphur was added Of such cystine, glutathione, methionine, thiamin and sodium sulphide rendered these waters fertile for this species or possibly strain, of diatom (Harvey, 1939)

Evidence has been obtained (H Rogers, private communication) of organic matter containing divalent sulphur in solution in inshore sea water, and Hutchinson (1943) has found 0 3 to 1 2 mg of thiamin and 3×10^{-3} mg of biotin per m^3 in a lake water

Sea water contains much sulphate, and experiments with a number of planktonic diatoms failed to show that this did not suffice for their growth although the addition of cystine or sodium sulphide had the effect of increasing the growth rate of several species In this connection it is of interest that other organisms prefer to take in their sulphur requirements as divalent sulphur Mast & Pace (1935) found that a colourless flagellate grew more rapidly in media where the sulphur was supplied as sodium sulphide or cystine than in media where it was in the form of sulphate

There is a possibility that other trace elements, besides iron and manganese, may at times occur in insufficient quantity for maximum growth of phytoplankton Some evidence suggesting this has been obtained by myself Of several trace elements necessary or beneficial to higher plants such as boron, zinc and copper, there is an ample supply in sea water, but of several others known to have some effect the quantities found by analyses (pp 31, 32) are below 1 mg per m^3, for instance, molybdenum and gallium *

The need for some organic constituent in the water was indicated in Allen s (1914) classic experiments on diatom growth in artificial sea water and I have obtained further evidence to the same effect Matsudiara (1939) found that the growth rate of two species of diatom varied markedly in waters collected from several positions and depths which had been enriched with nitrate, phosphate, silicate and iron He concludes that the differences are due to some organic substance

* Gallium is stated to be necessary for the maximum growth of *Lemna*, and Riley (1943) has observed that it stimulated the growth of *Nitzschia* in nutrient deficient culture media, but not when ample nitrate and phosphate were present

The production of plant life in South Atlantic waters has presented outstanding problems. Throughout the year the upper layers are well supplied with phosphates and nitrates in the southerly latitudes; the standing crop in summer varies enormously in different areas. There is no ascertained reason why the production should not be very much greater than it is.

A remarkably rich flora occurs in the deep ocean lying 20 to 120 miles off the island of South Georgia which rises steeply from the ocean floor; the standing crop in summer is some ten times greater than in the surrounding ocean, subject to similar hindering of growth by turbulence. In the Scotia Sea, fed by a current which has washed outlying islands of the Antarctic continent and passed over a submarine ridge, the standing crop is twice as great as elsewhere in corresponding latitudes. Hart (1941) attributes these heavy developments of plant life to a better supply of some constituent derived from land drainage, such as iron or manganese.

He also points out that, both in these rich areas and in those far from the influence of land drainage, the plants take out of the water many times more phosphate than is ever found present as phosphorus in the standing crop when it reaches its summer maximum, and considers that the latter is continuously subjected to very heavy grazing. In these seas control appears to be effected by (i) hindering of growth due to turbulence, (ii) grazing, (iii) lack of some constituent as iron or manganese supplied by land drainage, and (iv) short supply of silica on occasions. The first three could account for the observed distribution and quantities of phytoplankton.

The Magnitude of the Standing Crop of Plants

Early methods of sampling the standing crop of phytoplankton were to make comparable hauls with fine silk nets and count the organisms. Later, the volume of sea filtered by the nets was calculated and, more recently, it has been measured with an attached meter. In its various forms this technique allows a proportion of the smaller organisms to escape; the finest net has pores some $42 \times 50\,\mu$ when the silk is wet and swollen, yet when

it is drawn slowly through the sea it catches a considerable quantity of smaller organisms, many of which either occur in chains or have spines which entangle them. In some areas and at some times it undoubtedly catches the greater proportion of the plants, but in other areas or times it may give an entirely erroneous picture of the magnitude of the population. Another method has been to pump sea water through a hose from a series of depths and filter it; by this means of collection, counting the organisms and measuring the size of each species, comparable results have been arrived at. More recently samples of water obtained from a series of depths have either been centrifuged or have been poisoned, allowed to settle on the bottom of a cylinder, and counted from below with an inverted microscope. This sedimentation method has given considerably higher values than centrifuging and counting the cells in the deposit (Steeman Nielsen, 1933).

Such counts take a long time and the resulting tables of species and numbers can only be interpreted by an expert familiar with the various species as they occur in that area. The species vary greatly in size and in the proportion of plant tissue to sap within the cell. The size of individuals of a species varies (Wimpenny, 1936; Lucas, 1941; Gross, 1937); larger individuals of a diatom species are found in warmer than in colder seas.

A measure of the plants in a catch of mixed zooplankton and phytoplankton can be obtained by dissolving the plant pigments in acetone or alcohol and estimating either the mixed pigments or the chlorophyll. This technique has been used extensively; comparative estimates of net-caught plants have been made in the Barents Sea by Kreps & Verjbinskaya (1930, 1932), in the English Channel by Harvey, Cooper, Lebour & Russell (1935), in the Indian Ocean by Thompson & Gilson (1937) and in the Antarctic by Hart (1941).

Plants caught by filtering 1 to 6 litres of sea through paper or a collodion membrane have been estimated by Riley (1938–41) in various areas off the American coast and by Krey (1939) in Kiel Bay.

The colour in the yellow-green extract can be expressed in arbitrary units, since the quality of the colour is nearly always the same. In the English Channel the unit of plant pigments

has been linked with the quantity of phosphorus in the plants, and in the Gulf of Maine with the quantity of organic matter in the plants (correlation coefficient 0·76).

The carbon content of the flora lying below each square metre can be calculated for these two areas.

At a position in the English Channel with a depth of 50 metres, a particularly rich catch was made in March 1933 at the height of the spring outburst, when the netted plants contained some 7000 units of plant pigments per cubic metre of sea. This is commensurate with plants containing 0·025 g. of phosphorus and 1·5 g. of carbon below each square metre. The smallest catches were made in summer and midwinter. In summer the water contains very small organisms which would pass through any net, but observations by the sedimentation method indicate that the summer flora is only a very small percentage of that in the spring.

In the Gulf of Maine, Riley (1941) concluded that the flora below a square metre contained some 2 g. of carbon when at its maximum and a negligibly small quantity in winter. He filtered samples of water from a series of depths through no. 2 Whatman paper, which was found to retain 90 % or more of the organisms.

While considering magnitudes it is of interest to make a similar calculation for the extremely fertile ocean around South Georgia. In the upper 50 metres the net-caught plants below a square metre had an average content of some 1½ million units of plant pigments during the summer. If we assume the same ratio between plant pigments, phosphorus and carbon in these antarctic diatoms as have been found elsewhere, this indicates plants containing some 7·2 g. C per sq. metre.

These values can only be considered as very rough estimates of the quantity of carbon in plant protoplasm and food reserves at the season when the plant population is at its height. As with the estimates of annual production, they are first attempts to deduce the quantity, in absolute units, of the food supply of the fauna.

The Magnitude of the Annual Production

The first attempts to gain an idea of the annual production of organic matter by photosynthesis were made in the following manner from data obtained in the English Channel. The decrease in carbon dioxide and in phosphate in the water which took place between winter and early summer, when they were at a minimum, was found for a column of water below 1 sq. metre. These quantities had been built up into plant material during this period of the year, when the standing crop is at its greatest. How large a proportion of the annual production occurs during this period is unknown. No account could be taken of the carbon dioxide absorbed from the atmosphere or produced by respiration of animals and bacteria, nor of the phosphate regenerated during this period and utilized again. Similar calculations of production were also made from the decrease in nitrate in the water, and here also no account could be taken of the quantity of ammonium regenerated and used again as such. The quantities calculated are minimum values for production during the half year. Since the original calculations were made, reliable analyses of diatom plankton have been published which give the ratio of carbon to nitrogen to phosphorus in them, and these have been used to recalculate from the data of the original observers.

The increase in dissolved oxygen in the sea over this period, due to photosynthesis, has been used for similar calculations of production. This also takes no account of loss of oxygen to the atmosphere nor of oxygen used in respiration by bacteria and animals. It was assumed that the volume of oxygen evolved equals the volume of carbon dioxide assimilated—an investigation by Sargent & Hindman (1943) shows this ratio of unity to be substantially correct.

Analyses of plankton diatoms

		C	N	P
Redfield (1934)	Bay of Fundy	100	18·2	1·36
	Nova Scotia	100	15·6	2·26
Waksman *et al* (1937)		100	14·2	1·4
	Mean	100	16	1·67
Cooper (1937)	Mean ratio		16	1·96

Carbon produced by photosynthesis during half year below 1 sq. metre minimal estimates

	C g.
English Channel, from decrease in phosphate (Atkins, 1923)	53
carbon dioxide (Atkins, 1922)	84
carbon dioxide (Cooper, 1933)	101
phosphate (Cooper, 1938)	66
nitrate (Cooper, 1933)	39
English Channel, from increase in dissolved oxygen (Cooper, 1933)	60
Gulf of Maine, from decrease in phosphate (Riley, 1941)	40
Long Island Sound, from decrease in phosphate (Riley, 1941)	46

In Arctic waters Kreps & Verjbinskaya (1932) have made similar minimal estimates of production from phosphate data collected at intervals throughout a year in the Barents Sea. Here the greater part of the production is compressed into a relatively short period, from early May to mid-August. During this period the phosphate in the water decreased by some 1·1 g. P below each square metre, indicating the production of 66 g. C per sq. metre. During this period regeneration of phosphate was undoubtedly taking place, and the authors made a second estimate, allowing for this, on the assumption that it was equal to the increase in phosphate which took place in the water during the subsequent 100 days. This allowance suggests that the consumption of phosphate during the growing period was some $1{\cdot}1 + 0{\cdot}45 = 1{\cdot}55$ g. P, indicating the production of phytoplankton containing some 92 g. C below each square metre.

Another method of assessing annual production was evolved by Seiwell (1935) for waters of the tropical western North Atlantic, where a layer of oxygen-deficient water lies below the photosynthetic zone. He considered that this deficiency was due to the annual crop of organic matter being finally oxidized in this layer, and that the loss of oxygen was balanced by the supply from the water below and above brought about by turbulence. By assuming a value for the coefficient of eddy conductivity in this mid-water layer, the quantity of oxygen entering the layer was calculated. It was sufficient to oxidize 278 g. of organic carbon yearly below each square metre, and it

was considered that this value represented the annual production of organic matter. The argument depends upon two assumptions —the value of the coefficient of eddy conductivity and the assumption that the oxygen was utilized by decaying organisms which had fallen from above while the midwater layer was in these low latitudes. Evidence has since been advanced by Redfield that the low oxygen content is largely due to the decomposition of organisms which grew in it or fell into it when the water was much further north and nearer the surface in temperate latitudes. This suggests that the calculated value for production is too high, and in fact the calculated value is some four times greater than the minimal values calculated for the first half of the year in the English Channel, which is an area relatively rich in plankton and which would at first sight appear to have a very much greater annual production.

Gran (1927) and Marshall & Orr (1930) have suspended samples of sea water containing its natural flora and fauna in the sea, estimating the increase in oxygen after a period of time. Similar samples in black bottles were suspended alongside as controls, the final difference in oxygen concentration in the light and dark bottles giving a measure of the *gross* production by photosynthesis. In both light and dark bottles oxygen was being used in respiration by plants, bacteria and animals, so the difference in concentration of oxygen attained by the end of the experiment between the light and dark samples was a measure of the total photosynthesis; part of the organic matter produced by the plants was being lost continuously in their processes of respiration; this does not enter into the final result. It is the *nett* production, that is, the gross production less respiratory losses, which is required to obtain the annual production.

Measurements of gross production made by suspending samples of unfiltered sea water in light and black bottles have been continued by Riley (1938, 1939, 1941). The quantities of carbon synthesized annually below a square metre were calculated from a knowledge of the depth of the photosynthetic zone, and experimental data obtained at intervals during a year. These calculated quantities range up to 1000 g. C per sq. metre per year (Long Island Sound). From the quantity of chlorophyll contained in the plants, the respiratory losses were assessed, and

these deducted from the gross production gave tentative values for the annual production of phytoplankton—the carbon produced which is in excess of respiratory requirements and can therefore be used in the production of new material. This novel method of arriving at the desired result is very dependent upon a correct assessment of respiratory losses. Riley has also used the difference in both phosphate and nitrate content which arises between the light and dark bottles as a measure of the nett production. The measure is not strictly direct, since the plant organisms continue photosynthesis when the supply of either is reduced, building up storage products and attaining a phosphorus or nitrogen deficiency (Ketchum, 1939*b*).

The magnitudes of the tentative estimates based on these experimental methods are of interest.

Phytoplankton production (Riley, 1941)

		C per sq. metre per year (g.)
Long Island Sound	O_2 production	400–700
	P consumption	440–875
West Atlantic 23–41° N.	N consumption	140–365
Georges Bank, Gulf of Maine, O_2 production		C per sq. metre per day (mg.)
	Jan.	−50
	March	190
	April	950
	May	540
	June	630
	Sept.	140

Riley has concluded that no very great difference exists between the annual production in deep ocean waters of the tropics and in temperate latitudes, where insufficient light reduces growth during the winter. He points out that, although phytoplankton is sparse in tropic waters, the low concentration of the breeding stock is partly counterbalanced by the great depth of the photosynthetic zone. The concentration of nutrients is kept very low by rapid utilization rather than by lack of available supply. Seiwell's calculation points in the same direction as Riley's conclusion, which is based on his own data of the rate of plant production in the Sargasso.

This view is opposed to the usual conception that deep tropical and subtropical oceans, away from land or upwelling water, are relatively barren wastes. Where comparable net hauls have been made vertically through the upper layers they have caught only a small fraction of the quantity of animals which are caught in temperate or high-latitude oceans. After making allowance for the seasonal changes in animal population in the latter areas, there is still a smaller average animal population in low latitudes. In these warmer seas the metabolic rate of the animals is doubtless greater—the temperature difference may be of the order of 20° C.—and a similar population would require a greater annual production of plant food. However, the extent of this extra requirement may not be great; Fox & Wingfield (1937) give instances where the oxygen consumption of some species of marine animals is less at the same temperature for individuals which have been collected from a warmer environment than for individuals collected from colder waters.

Consumption of Phytoplankton by Animals

The standing crop or breeding stock of phytoplankton is always in the process of being depleted by herbivores, but the incidence and intensity of this grazing is irregular. The abundance of herbivores, for the most part copepods, changes throughout the year; brood of any one species follows brood at intervals of weeks or months. Moreover, they occur in swarms. In their early stages these herbivores are small in comparison with most of the diatoms which compose the bulk of the phytoplankton in temperate regions, and the kind of food they subsist on then is unknown. In some localities there are many minute flagellates and minute diatoms in the water, but this is not so everywhere. Survival and growth to a size when the herbivores can eat average-sized phytoplankton, such as is caught in a tow-net in most seas, will depend largely on the supply of food during these early stages.

The drastic effect of grazing on the plant population is apparent from the following illustration: When a population of 100 plants per litre makes six divisions, the population rises to 6400 per litre; if, however, one plant in every ten is eaten during

the intervals between each division, the population will rise to 3400 per litre, 413 having been eaten. This light grazing almost halves the population attained after six divisions have been made.

Where and when herbivores of a diatom-eating size are numerous, there we would expect diatoms to be sparse and vice versa. This inverse relationship has been found to occur in several areas (Harvey, Cooper, Lebour & Russell, 1935; Wimpenny, 1936; Bigelow, Lillick & Sears, 1940; Mare, 1940; Hart, 1941). On the other hand, Steeman Nielsen (1937) has found areas where large quantities of both zooplankton and phytoplankton exist simultaneously throughout a considerable period.

Hardy & Gunther (1935) have advanced a theory that zooplankton avoid areas rich in diatoms, and suggest that the animals do not rise at night into the upper layers, as they normally do, until currents carry the diatom-rich patch in the water above away from them. As a result of this 'animal exclusion' the animals and plants of the plankton would become distributed in alternate communities. However it may come about, such a distribution in alternate communities appears to be more usual than otherwise.

The density of phytoplankton often increases very rapidly, a spectacular rise in numbers taking place in a few days, particularly during the spring outburst in temperate seas. On the other hand, the rise in numbers of copepods of diatom-eating size depends upon conditions which existed while they were passing through their earlier stages some weeks previously and upon the proportion of carnivores which normally prey upon them. Thus the actual number of these later stage copepods present at any time depends upon past conditions, a factor which has been particularly stressed by Steeman Nielsen (1937) and by Clarke (1939). The effect of grazing herbivores on the plant community is brought about in a few days, whereas the effect of phytoplankton production on the abundance of herbivores depends upon a food supply during previous weeks or months; they are two different and quite distinct considerations.

Reverting to the effect of grazing, it was observed that the sudden diminution in numbers of diatoms at the end of the

spring outbursts of 1933 and 1934 in the English Channel occurred at a time when the larger copepods had commenced to increase rapidly. At these times the water contained many faecal pellets of copepods coloured green with chlorophyll. The larger copepods are extremely voracious. I have watched a late stage *Calanus finmarchicus*, kept moving in a suspension of diatoms, which discharged green faecal pellets at 20 minute intervals.

The observations made during these two years indicated that the sudden cessation of the vernal diatom outburst, which took place before half the available nutrient salts had been utilized, was due to their being eaten. The only series of quantitative observations of both phytoplankton and herbivores during the spring outburst in other areas is in Long Island Sound by Riley (1941, 1943). He concluded that the sudden cessation of the outburst cannot have been due to grazing, but more likely due to the diatoms having become 'senescent'—a term used to denote their physiological state when they cease dividing in culture media which still contain all their necessary requirements as far as is at present known.

The sudden cessation of the spring outburst, usually composed of several species of diatoms, is common in temperate regions and takes place well before the available nutrient salts are used up. The cause of this cessation may be consumption by animals, as appears to have taken place in the English Channel, or a change in the 'physiological state' of the plants, such as has been observed in Lake Windermere, or lack of some necessary chemical constituent in the water. That cessation in the English Channel is not due to lack of some minor constituent, with the possible exception of iron, is indicated by the following observations.

If sea water collected during spring, or early summer, is enriched with iron and some twenty times more nitrogen salt and phosphate than it ever contains normally during the winter maximum and kept in the light, the diatoms present increase. If washed and filtered air is blown through the water, the growth of diatoms uses up all these added nutrients. The composition of the crop is similar to the composition of phytoplankton in the sea; the dominant species remain dominant and those which were less plentiful do not appear to be crowded out (Harvey,

unpublished). It yet remains to be determined whether water from the open sea contains sufficient iron to produce such heavy growths.

Some experiments have been made on the rate at which late-stage *Calanus*, a particularly frequent herbivore, grazes on suspensions of diatoms of varying concentrations, mostly more concentrated than would occur in the sea. This animal collected in 1 hour all the *Nitzschia*, a very small diatom, present in 0·2 c.c. of the water, irrespective of the concentration of the diatoms. With two species of larger diatoms it collected those in *circa* 3 and 8 c.c. respectively (Fuller, 1937; Harvey, 1937). It thus appears that this herbivore can filter minute organisms from a limited quantity of water and can also catch larger organisms dispersed in a much larger quantity of water. With reference to the products of digestion Gardiner (1937) has observed the rapid liberation of phosphate by *Calanus* feeding on diatoms, and Cooper has found that the faecal pellets contain very little phosphorus compared with uneaten diatoms. The nitrogen is probably excreted mostly as ammonia, but how much is digested and how much left in the pellets is unknown.

In the older literature there appears a tacit assumption that the majority of phytoplankton organisms die and sink, and that in temperate seas there is a continuous rain of dead diatoms falling on the bottom. That this does occur in some areas is known, but in one such area Moore (1931) has shown that the quantity of diatoms reaching the bottom is greatly exceeded by the quantity of green faecal pellets. I am indebted to Dr T. J. Hart for the information that the diatomaceous ooze lying on the sea floor of considerable areas of the South Atlantic below very deep water consists of much-broken frustules, and is in appearance compatible with their having been eaten and voided by euphausids in the upper layers. It seems indeed likely that the fate of most phytoplankton organisms is to be eaten before reaching the bottom, particularly in deep water.

The digestion of the plant cells and the subsequent history of the solid excreta are links in the food chain which merit investigation. Doubtless particles of food, which have not been fully digested by the herbivores which have dined first, are invaginated by flagellates and ciliates, and eaten by other zooplankton.

There are periods during the summer when phytoplankton is particularly scarce, small larvae and other zooplankton are at their greatest concentration, and many fragments of organic matter are suspended in the water. During these periods it is not obvious how the numerous zooplankton obtain sufficient food unless this organic detritus is eaten. It has been observed that during such periods the faecal pellets change in colour from green to brown, suggesting that the diet contained a higher proportion of organic detritus (Mare, 1940).

In considering the effect of animals on plant production, it is axiomatic that the maximum possible fertility will coincide with a balanced population of carnivores, herbivores and plants. In the sea each occur patchily both in time and space, so a lack of balance is the usual condition. A departure from balance in any one of the three directions cannot persist, but will in time not only right itself but probably swing in the opposite direction.

Fluctuations in Production of Plants and Animals from Year to Year

Russell (1935) has taken comparable hauls with a net at weekly intervals throughout a number of years at a position in the English Channel. He observed a relation between the numbers of young fish which had been spawned in the summer and survived their early larval stages and the 'winter maximum' of phosphate in the water at the beginning of the year. The figure taken from data published by Cooper (1938) shows this relation very clearly. The lower 'winter maxima' which occurred during the 1930's were also coincident with a change in the type of plankton (Russell, 1936), a *Sagitta setosa* community replacing a denser average population characterized by *S. elegans* (Fig. 29).

The marked difference in winter maxima of phosphate and general fertility between the 1920's and 1930's is not reflected in any well-marked change in the temperature and salinity of the water during the transitional year or years. The concentration of a conservative constituent of the water, as the salinity, indicates its physical history, whereas the winter maximum of phosphate indicates its biological history. Judging by these relations found by Russell, it also appears to indicate the water's biological future in this area.

Fluctuations in fish populations where the great commercial fisheries operate have been the subject of investigation for many years. Rapid progress has been made during the last two decades, so much so that it is now possible to gauge the effect of intense fishing in an area and, indeed, to gauge the extent of fishing which would give the maximum return for human effort without unduly depleting the stock. The effect upon the future fish population of particularly good brood

FIG. 29. Deviation from the mean winter maximum of phosphate and from the mean number of summer-spawned young fish for years from 1924 to 1937. The black columns above and below the horizontal line denote the extent to which winter maximum of phosphate each year exceeded or fell short of the mean for the 12 years. The outlined blocks show the extent to which the average number of young fish caught per haul each year exceeded or fell short of the mean value for the 12 years.

years, when an abnormal proportion of the young survive, has allowed a forecast to be made for a year, or even more than a year, ahead. Coincident with fluctuations brought about by intensity of fishing and good or bad brood years in the populations of particular kinds of fish, there are fluctuations arising from a general change in the fertility of an area, such as took place in the English Channel between the 1920's and the 1930's. The relation found by Russell, between fertility of the area and the winter store of phosphorus in the water, is a definite step towards elucidating this third factor.

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